Detection and Removal of Molten Salts From Molten
Aluminum Alloys

Final Report

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Selee Corporation
Hendersonville, NC

FINAL PROJECT REPORT

DETECTION AND REMOVAL OF MOLTEN SALTS FROM MOLTEN ALUMINUM ALLOYS

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1.0   INTRODUCTION

Salts formed as a byproduct of chlorine injection during the casting of aluminum have been identified as one source of inclusions and defects in ingots and cast shapes[1.] Moreover, the salts have been shown to reduce the efficiency of filters designed to remove solid inclusions from the metal stream. The use of fluxing gases is described in more detail in Appendix IV.

Sell Corporation proposed two new tools to help aluminum producers deal with the problems related to salts.   One was a simple probe that indicated in real time that excess salts were present.   The other was a salt filter that would selectively remove liquid salts from the liquid metal stream.

A diagram of the probe is shown in Figure 1.1.   It consists of an electrically conductive silicon carbide rod, part of which is coated with a porous ceramic layer. The porous ceramic material is not electrically conductive and is not wetted by the molten metal. It is, however, wetted by molten salts.

Figure 1.1: Drawing of Probe

SALT PROBE

CONDUCTIVE
SILICON CARBIDE ROD

MICORPOROUS COATING
NOT WETTED BY METAL
WETTED BY SALT

MICROPOROUS COATING
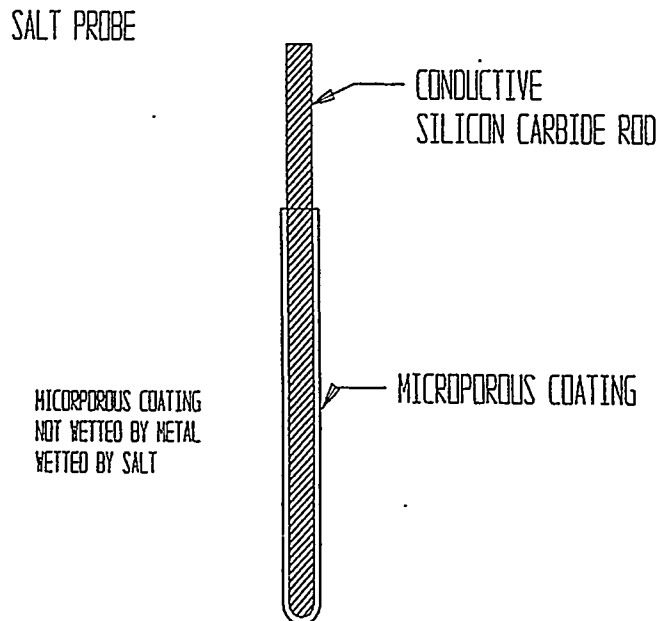
To test for the presence of salt in a molten aluminum alloy stream the probe is partially immersed in the metal.   An uncoated rod is also immersed, and the two are connected by an electrical circuit as shown in Figure 1.2.

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Figure 1.2: Drawing of Probe Circuit

SALT DETECTOR CIRCUT
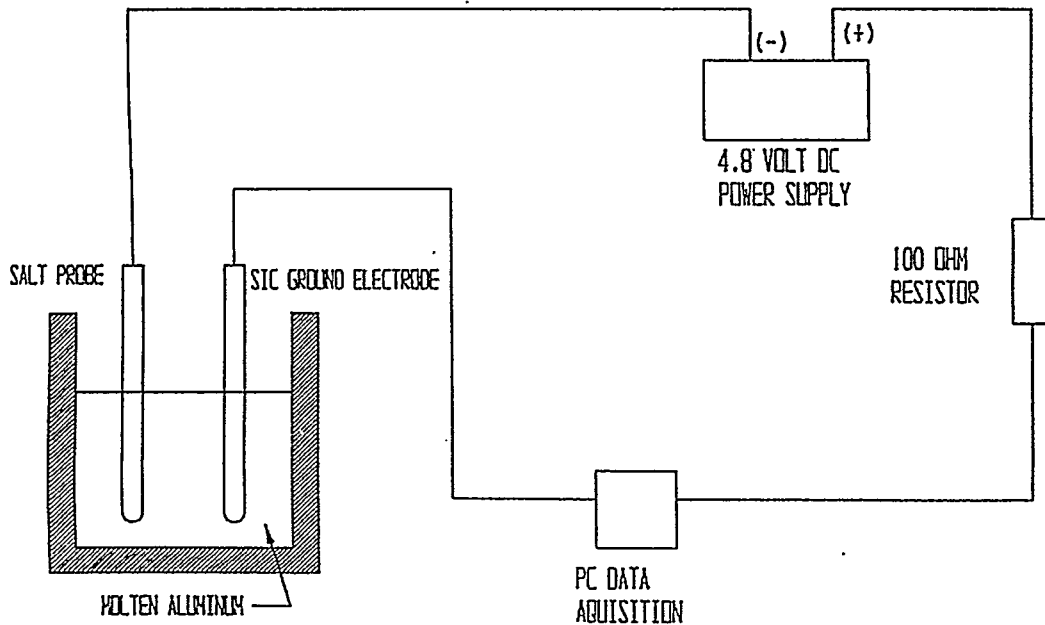
If no salt is present the alloy does not penetrate into the pores of the coating. Thus the electrical circuit remains open and the resistance between the probe and the grounding electrode remains very high. Molten salt does penetrate the pores of the ceramic coating. It forms an electrical bridge and over time the resistance between the probe and the grounding electrode will decrease to nearly zero. A typical positive probe response is shown in Figure 1.3.

Figure 1.3: Typical Probe Response
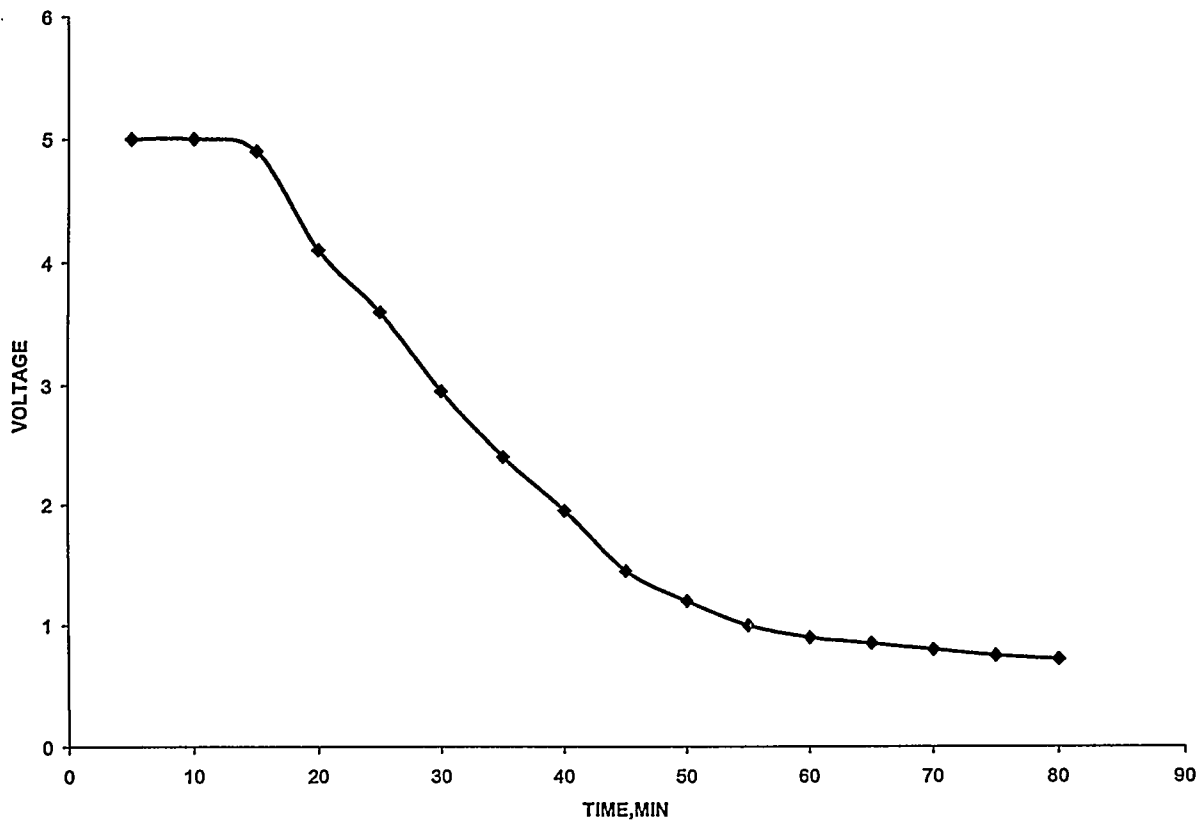
The salt filter media was made from a ceramic composition very similar to the material used to coat the rods. It had high pore volume with pore sizes less than 150 microns. Since the material is not wetted by the molten metal, the metal does not penetrate into the pore structure. The molten salt, however, does wet the surface and so it is readily worked in. Thus, a means is provided to selectively remove molten salt from the metal stream.

Although both of these concepts had been shown to work in lab scale experiments, experience was needed in flowing streams of metal. In particular the objectives of this project were:

a) To define the best coating thickness for the probes
b) To correlate the probe response with the level of chlorine injection and with the measured amount of salt in the metal.
c) To determine the consistency of the probe response.
d) To optimize the pore size distribution of the salt filter.

e) To optimize the size of the salt filter media.
f) To measure the filtration efficiency of the media.
g) To estimate the adsorptive capacity of the media.
h) To find if the use of the media caused any operational problems in the normal casting process.

The experimental caster at the Alcoa Technology Center was an ideal venue for testing since the metal could be cast under highly controlled conditions that were representative of commercial cast shops. At the same time, the amount of chlorine injected into the metal could be varied over a wide range. The technical expertise of the Alcoa personnel was essential for controlling the casting conditions and especially for operating the LIMCA II and understanding the data.

2.0   EXPERIMENTAL ORGANIZATION AND STRATEGY

In general the experimental strategy was to cast a high magnesium alloy which is the kind most prone to salt related problems. The amount of salt was controlled by metering different amounts of chlorine into the rotary degasser. Various types of salt media and conventional filters were used in the metal stream. Salt probes were placed both up stream and down stream from the filters. In addition to the salt probe response, the metal cleanliness was also evaluated using a LIMCA II, LAIS sampling, and chemical analysis of chill mold samples. All of these measurements were also done upstream and downstream of the filters to evaluate their removal efficiency. LIMCA II run charts are all included in Appendix I.

For most of the experiments the salt adsorption media was made in the form of pellets, either 3 or 7 mm in diameter. In order to expose the metal to a bed of these pellets a special filter bowl, shown in Figure 2.1 was used. Two conventional ceramic foam filters were used, one above and one below the bed of pellets. The bowl was made with a continuous taper so that the size of the ceramic foam filters could be changed if desired. Previous experiments with dual stage filter bowls had shown that such a system could be preheated and run with no special problems. The addition of the salt media was, of course, a new variable.

A Selee HVB burner was used to preheat the filters and bowl before the cast.

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Figure 2.1 : Drawing of the Filter:
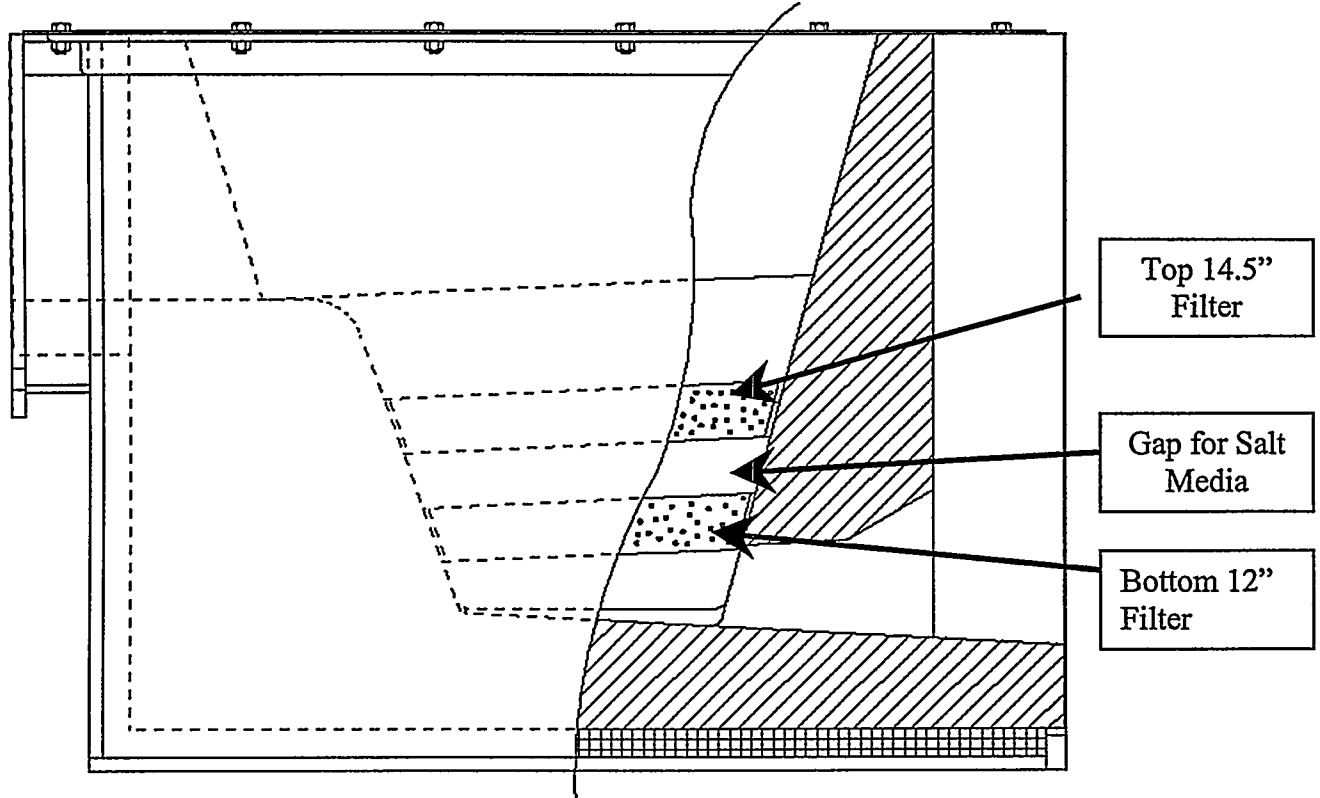
Figure 2.2 is a flow diagram of the experimental set up at the Alcoa Technology Center. The metal was melted and alloyed in a holding furnace. Once the cast was started the metal flowed from the furnace to a single rotor degasser. Argon was injected through the rotary degasser along with the chlorine. The amount of argon was held constant while the amount of chlorine was varied as will be described in greater detail. In the first set of experiments, one set of salt probes was located between the furnace and the degasser. LAIS samples and chill mold samples were also taken at that point. For later experiments this was discontinued in favor of collecting more data down stream.

Figure 2.2: Drawing of Experimental Set-Up

EXPERIMENTAL
CASTING
SET UP
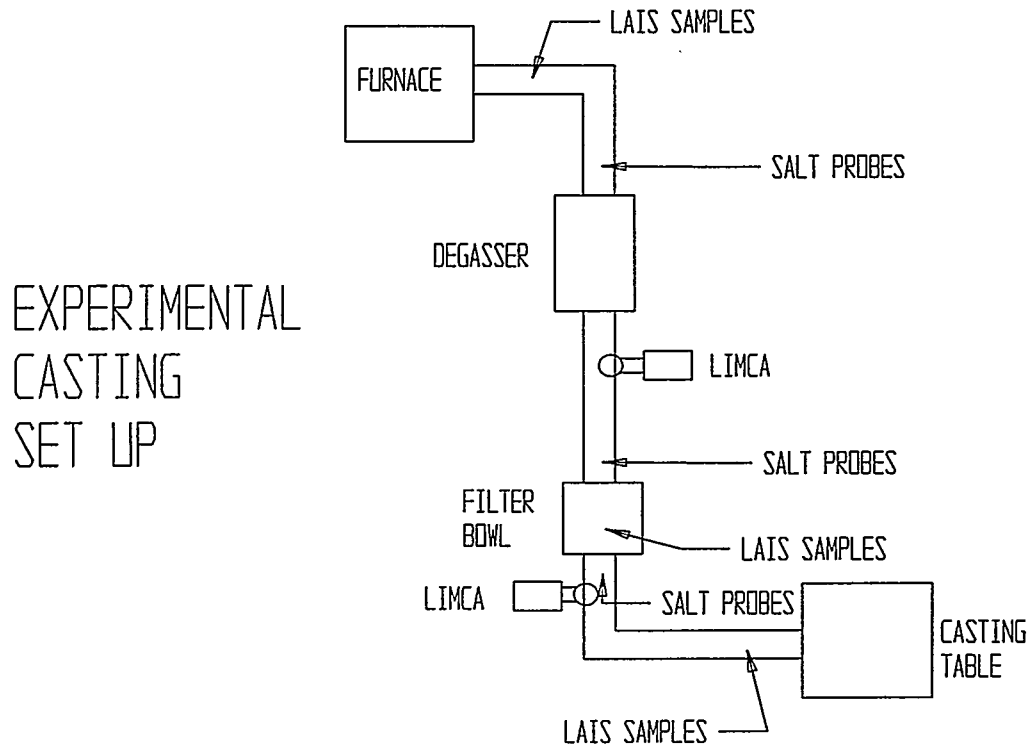
From the degasser the metal flowed to the filter bowl described above. Between the degasser and filter bowl were sampling points for LIMCA II, LAIS, chill mold samples, and salt probes. Likewise the metal was evaluated just downstream from the filter bowl as well. Figures 2.31 through 2.33 show photographs of the experimental setup.

The experimental conditions are shown in table 2.4.

Figure 2.31: Filter bowl with bottom filter in place.

Figure 2.32: Filter bowl with bottom filter and salt media added.

Figure 2.33: Filter bowl with all filter media and vent tube ready to preheat.

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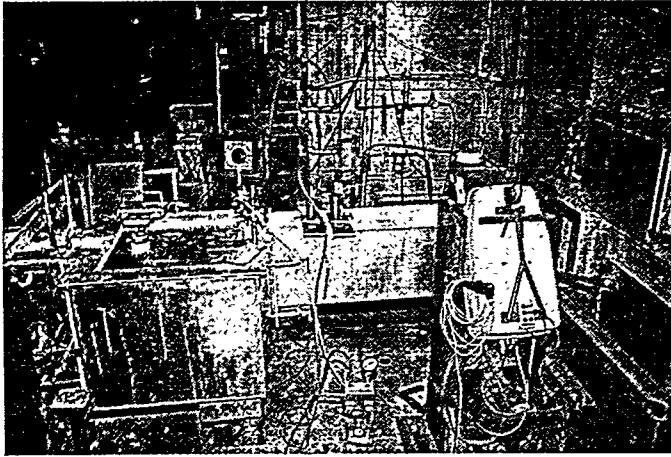
Figure 2.34:   Experimental setup – Filter bowl and upstream
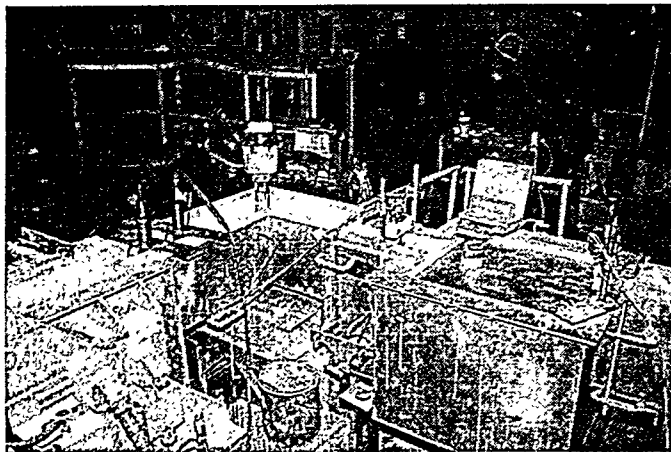
Figure 2.35:   Experimental setup – Filter bowl and downstream.

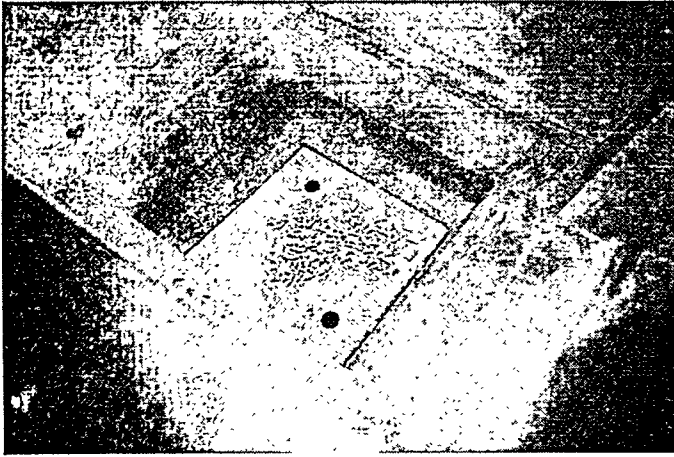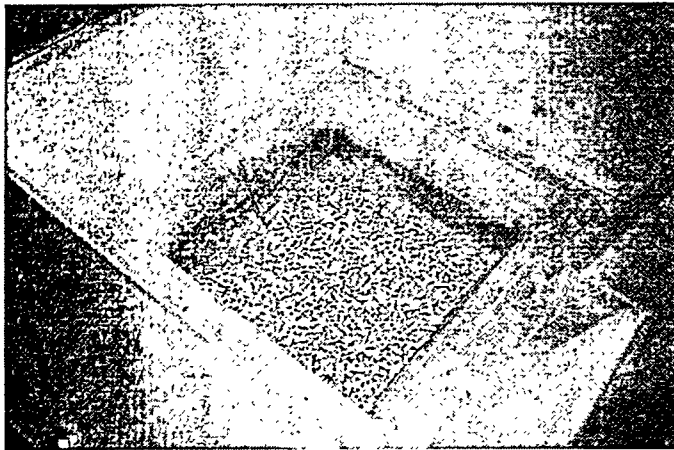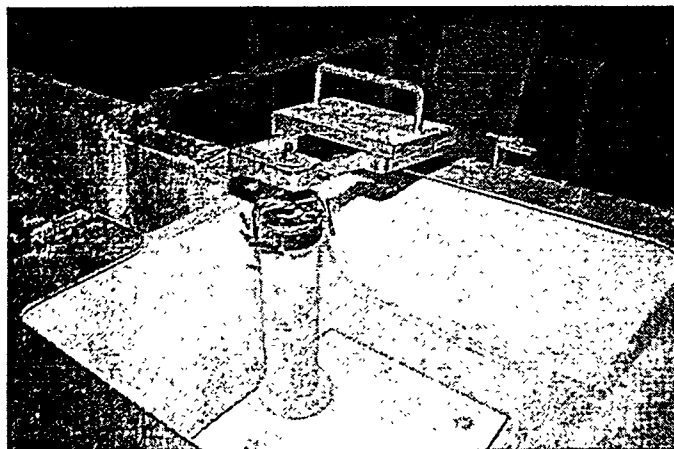**Table 2.4:**

TEST PARAMETERS	
Alloy	5182[1]
Casting rate	10,800 Lbs/hr.
	2 in/min
Ingot Size	16 x 16 x 160 in.
Foam Filter Size	12/14.5 in.
Filter Factor	1.82 lbs/in^2/hr.
Degasser[1]	Single Stage 622
Rotor Speed	160 rpm
Argon Injection	100 scfh
CL$_2$ Injection	0-8.0 scfh
* Degasser was flushed in the mornings before 1st cast of the day.	
Furnace Fluxing	Stir .75 hrs. before cast
Grain Refiner	None (with 2 exceptions)
Inclusion Sampling	Limca II
	350 µ Oriface
	Aluminosilicate Tubes
Furnace Description	25 ton bottom pour reverberatory furnace

[1]Specific chemistry is shown in Appendix II

The alloy was chosen because of its high magnesium content (see Table 2.5) and because of its commercial importance. With the exception of the chlorine content, which was high to very high, most of the other parameters represent more or less normal operating conditions.

Table 2.5: Alloy Specification: AA5182: Can-End stock

Registered Designation	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Others Each	Aluminum Total	
5182	0.20	0.35	0.15	0.20 – 0.50	4.0 – 5.0	0.10	0.25	0.10	0.05	0.15	Remainder

Table 2.6: Pore Size Distribution

	1st Experimental Set, Large Pore	1st Experimental Set, Small pore	2nd Experimental Set	3rd Experimental Set, Boron Nitride	3rd Experimental Set Frit/Alumina
Sample ID	SF003	SF004	SF006	SF016	SF014
Total Intrusion volume, cc/gm	0.46	0.53	0.54	1.2	0.45
Total Surface area, m2/gm	13	18.8	19.4	235	6.23
Median pore diameter, microns	17.14	18.1	22.8	5.53	0.28

3.0   FIRST SET OF EXPERIMENTS

3.1   Independent variables

The independent variables were:

Chlorine injection rate: This was planned to be at levels of 0.25, 4 and 8 SCFH.   Each cast was started with no chlorine injection in order to establish a baseline. Once a few data points from both of the LIMCA II units (upstream and downstream from the filter) were established, the chlorine injection was started. This generally occurred about half way through the cast.

Salt media vs. no salt media: In some cases the cast was made with only conventional ceramic foam filters with no salt adsorption media present.

Salt media pore size: Pellets with two different pore sizes were used. Table 2.6 shows the mercury porosimetry data of these pellets along with the salt media used in later tests as well.

Salt media pellet size: As described earlier, most tests were done with the salt adsorption media in the form of extruded pellets. The pellet diameter was of interest because it would indicate if the exposed surface area of the media made a difference in performance. This in turn could indicate what limited the filter efficiency: mass transfer, or the intrinsic removal capacity of filter media.

Although these were the main variables to be investigated, there was also interest in obtaining a little data on two more points. One was the concept of making the salt adsorption media in the form of ceramic foam rather than pellets. A ceramic foam plate would be easier to use and would provide still more surface area than small pellets.   The disadvantage to using ceramic foam is that, owing to its low density, there is simply less filter media present.

The other point of interest had to do with grain refiner.   The metal for these tests was remelted and reused each day.   Grain refiner was not used for most of the tests because it might have a tendency to build up over time.   Grain refiner was run for the last two trials just to get an idea of its effect.

3.2   Results and Discussion

Pattern of LIMCA II Data:

Figure 3.2 shows a typical LIMCA II run chart from this set of experiments. A complete set of run charts can be found in Appendix 2. Figure 3.2 shows the N-20 values before the ceramic foam filter (BCFF) and after the ceramic foam filter (ACFF). The N-20 number refers to the number of particles per kilogram greater than 20 microns. Note that the N-20 of the unfiltered metal was about 5 thousand at the beginning of the cast. At about 43 minutes into the cast the chlorine was turned on and the N-20 before the filter quickly jumped to a much higher level.

Figure 3.2: Typical Limca Run Chart

Cast Number 770348, Experiment 10, Pellet Lot 3B
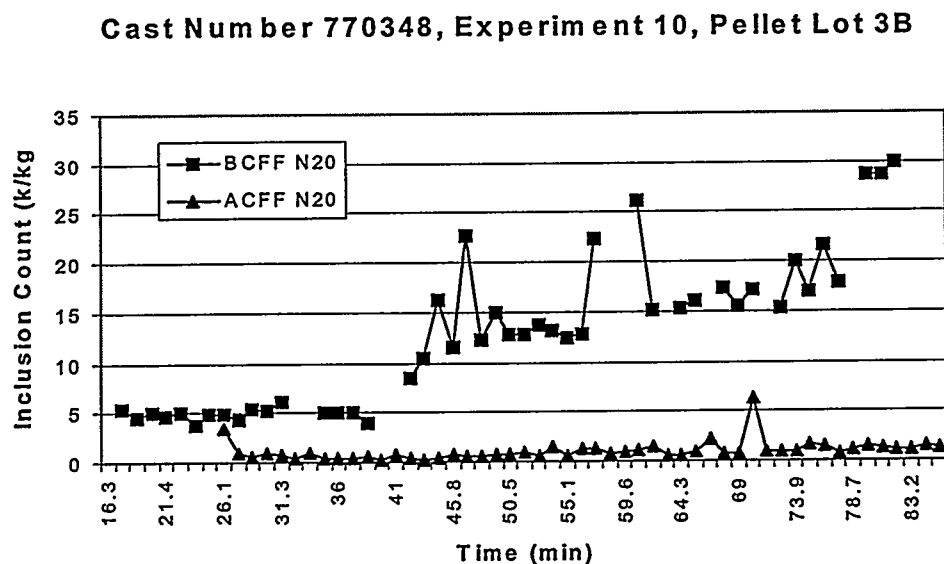
The N-20 after the filter is much lower both before and after the chlorine was turned on, as would be expected for a system with a fairly high filtration efficiency.

Data Summary

Table 3.1 is a summary of the measurements made in this set of tests. Each experiment is broken into two parts: "a" refers to before the chlorine was turned on and "b" refers to after the chorine was turned on. In addition to the N-20 data from the LIMCA II, the LAIS results are also shown. LAIS is a qualitative as well as quantitative method of evaluating the cleanliness of an aluminum alloy based on drawing a sample of the liquid metal through a fine frit. Also shown are the few GDMS data points. GDMS stands for glow discharge mass spectometery. This is a method especially suited for measuring very low concentrations of chlorine.

Table 3.1 Raw Data from First Run – LiMCA, LAIS, and gdms

Drop #	Conditions (1=small; 2=large)				Before Filter			After Filter		
	Cl ft3/hr	Pore	Phys	Ppm Ca	N20	LAIS	gdms	N20	LAIS	gdms
770349	0	2	2	41	5.1	0.079		0.50	0.008	
770349	0.25	2	2	41	5.62	0.006		0.60	0.025	
770341	0	1	1	47	5.44	---		2.02	---	
770341	4	1	1	47	10.05	0.625		2.76	0.188	
770339	0	2	1	39	5.90	0.131		1.4	0.023	
770339	4	2	1	39	10.57	0.213		5.94	0.035	
770347	0	2	1	21	5.98	0.094		0.62	0	
770347	4	2	1	21	8.04	0.132		0.50	0.013	
770338	0	1	2	21	5.4	0.185		3.5	0.066	
770338	4	1	2	21	16.18	0.208		4.19	0.127	
770342	0	2	2	47	5.32	---		1.17	---	
770342	4	2	2	47	8.66	0.447		0.68	0.005	
770343	0	1	1	28	5.01	0.415		0.45	0.004	0.06
770343	8	1	1	28	15.3	0.630	10	1.69	0.093	5.9
770344	0	2	1	28	4.67	0.420		0.11	0.163	
770344	8	2	1	28	12.53	0.898		0.50	0.158	
770348	0	2	1	21	4.91	---		0.83	---	
770348	8	2	1	21	17.20	0.627	12	1.07	0.105	5
770345	0	1	2	21	5.15	0.116		0.61	0.034	0.35
770345	8	1	2	21	16.26	0.501	14	1.82	0.016	4.3
770346	0	2	2	21	5.44	0.078		0.35	0.030	0.30
770346	8	2	2	21	14.85	0.528	63	1.07	0.114	1.3
770337	0	None	---	31	9.7	0.692		5.1	0.382	
770337	4	None	---	31	12.93	0.191		5.7	0.470	
770351	0	None	---	37	6.18	3.973		0.82	0.018	
770351	4	None	---	37	13.12	0.435		1.21	0.022	
770340	0	None	---	39	8.3	0.107	6.5	1.0	0.025	2.4
770340	4	None	---	39	13.63	0.386		3.42	0.074	
770352	0	None	---	37	---	---		---	---	
770352	4	None	---	37	19.99	0.701	5.3	2.11	0.038	13
770350	0	2	2	41	---	0.307		---	0.065	
770350	4	2	2	41	9.24	0.453		0.63	0.142	
770353	0	Plate	--	17	4.68	0.554		---	0.042	
770353	8	Plate	--	17	18.68	---		2.41	---	
770354	0	Plate	--	17+TiB2	7.98	---		4.24	---	
770354	8	Plate	--	17+TiB2	31.61	0.417		11.16	0.025	
770355	0	2	2	6+tiB2	7.50	---		1.16	---	
770355	8	2	2	6+TiB2	28.79	---		4.77	---	
770356	0	2	2	6+TiB2	8.69	0.256		2.83	0.009	
770356	4	2	2	6+TiB2	28.42	---		3.78	---	

Experimental Problems

As with almost any large complex experimental program certain problems were encountered. Data from the first few runs looked suspiciously high compared to other samples taken under similar running conditions. This is especially true of the first two runs, experiments 13 and 7. (The cast numbers shown in table 3.1 are sequential and can be used to establish the chronological order of the tests.) Qualitative analysis of the LAIS samples showed that this was caused by the presence of a large amount of grain refiner in the starting metal. This was filtered out after the first few casts and numbers remained relatively low until grain refiner was intentionally added in experiments 19, 20, and 21.

Unfortunately this made the analysis of the first factorial design at the chlorine injection rate of 5 SCFM impossible.

The other possible error was the level of calcium in the metal. For most of the runs it was in excess of 20 ppm and going as high as 47 ppm. The normal level is about 6 ppm. The extra calcium was added to try to make chemical analysis of the chlorine easier. However, at the casting temperature calcium chloride is a solid. This may have effected the interaction with the filter and probe, which are designed for molten salts.

Factorial analysis

There are many possible ways to analyze this set of data. Of particular interest was the question of which of the versions of the salt filter media worked the best. Table 3.3 shows an analysis of the sample run at an injection rate of 8 SCFH. The second column focuses on the N-20 numbers. The number for large pore filters is considerably smaller than for fine pore filters, suggesting that the large pore filters were more efficient. The diameter of the pellets had a much smaller effect. Runs made with salt media averaged much lower than runs without media (recall that these runs still had conventional ceramic foam filters in place). The few runs done with the filter plate, in other words, the salt media in the form of a ceramic foam filter, were better than no salt media, but not as good as the pellets.

The next column shows the same sort of analysis using C-20 as the dependent variable. The C-20 is based on the volume of particles greater than 20 microns rather than just the number. This gives much greater weight to the larger particles, which, as a practical matter, are more likely to cause problems. The same sort of pattern is seen in this case: larger pore filters were better than fine pore filters; the diameter of the pellets did not have much effect; runs with the media were much better than runs without media; and plate filters were not as good as the pellets.

The next column is the N-20 data expressed as % reduction, and shows more or less the same pattern as does the LAIS data.

Table 3.3: Analysis of Effect

Factorial Analysis					
Salt Filter Media	LiMCA N20 After Filter	LiMCA C20 After Filter	N20 % Reduction	LAIS % Reduction	Particles >50 Microns
Large Pore	1070	18.5	95.17	80.5	1
Small Pore	1755	29	88.5	90.5	1
Difference	-685	-10.5	6.67	-10	0
Large Diameter	1445	24	90.7	87	1
Small Diameter	1380	23.5	92.97	84	1
Difference	65	0.5	-2.27	3	0
Average with Media	1413	23.7	91.8	85.5	1
Average without Media	2765	65	53.9	31	4
Salt Filter Plate	2410	28	NA	NA	1

LAIS Qualitative Analysis

Figures 3.5a and 3.5b show a typical LAIS frit from this experiment. In general the samples were about as expected. They showed large amounts of salt upstream from the filters, with smaller amounts downstream. There were usually oxide particles associated with the salts. The only unusual finding was the presence of grain refiner in the first runs as described above.
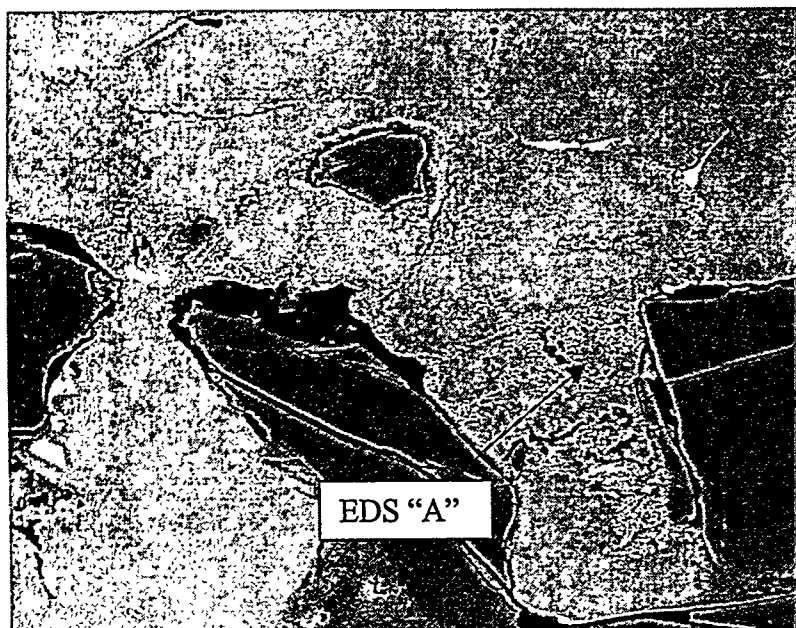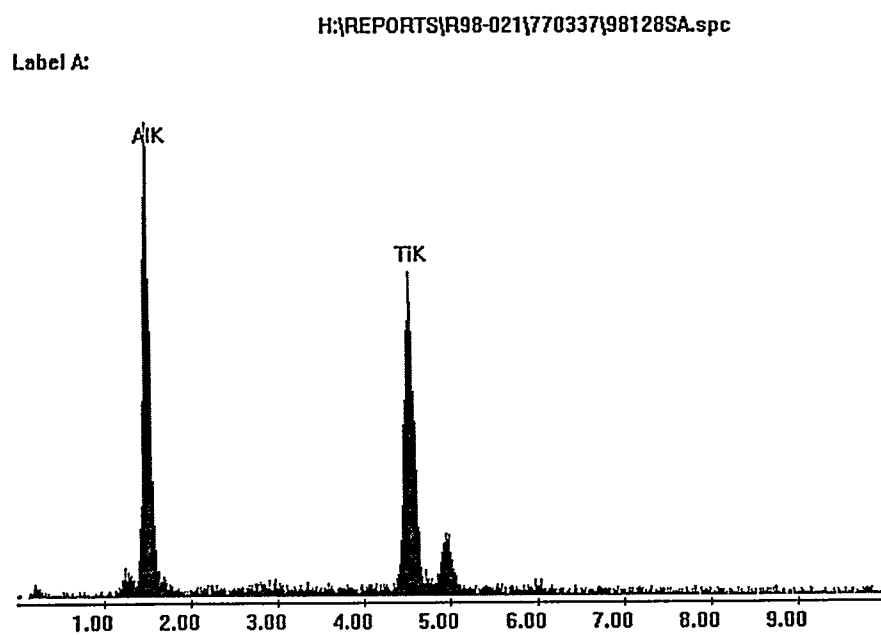
EDS "A"

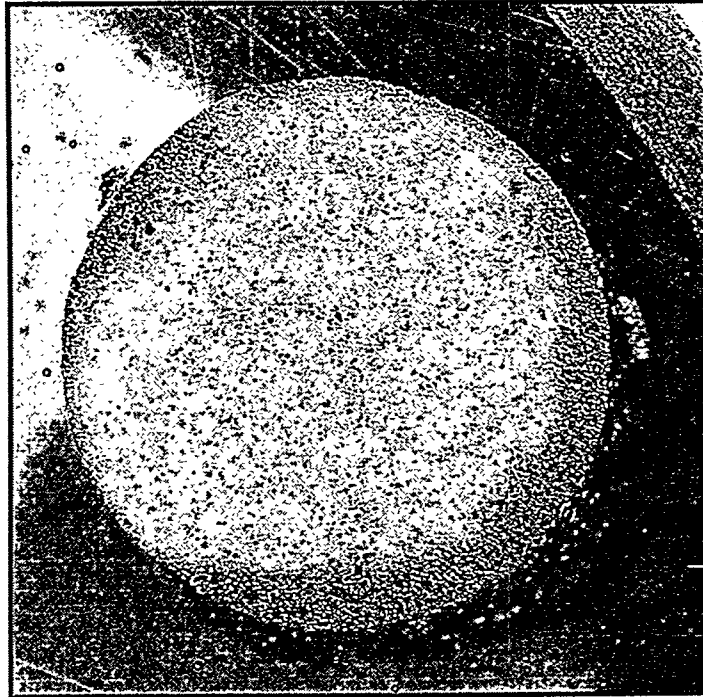Figure 3.5a

Label A:

Figure 3.5b

Figure 3.4: **Photograph of Salt Media showing reaction zone near surface of the pellet**
(First set of experiments)

Other Conclusions and Observations

a) *There was good correlation between the amount of chlorine injected and the LAIS data before the filter.*

b) *There was good correlation between the amount of chlorine injected and the N-20 LIMCA II data before the filter.*

c) *There was no trend between morning and afternoon runs. There had been some concern over this point. The furnace held enough metal for two drops. The pattern was to do one drop in the morning and another in the afternoon. There was some concern that impurities would tend to settle or float during the day. This did not prove to be the case.*

d) *There was very poor correlation between the LAIS and the LIMCA II data.*

e) *GDMS seemed to work very well for this study as it correlated over a very wide range with the amount of chlorine injected.*

f) *GDMS showed about 82% reduction of chlorine when salt media was used.*

g) *The salt adsorption media turned a black color on the surface when exposed to salts in the metal. (See Figure 3.4) Likewise, the salt probes that reacted and became conductive all had at least one black spot present. The chemistry of this color change is not understood. It is also interesting to note that the black spots on the probes tended to be at or near the bottom end of the probes in spite of the fact that the salts float in the metal.*

h) *The addition of the pellets to the metal stream caused no problems with the preheat or normal operation of the casting line.*

i) *Several of the LIMCA II run charts showed an upward trend near the end of the cast suggesting that some longer term effects may appear with longer run time.*

4.0 SECOND SET OF EXPERIMENTS

Several variables were investigated in the first set of experiments. The strategy for the second set was to reduce the number of variables and perform more repetitions to gain a higher degree of confidence in the results.

The experimental equipment and configuration were much the same as for the first set. Sampling upstream from the degasser was discontinued, as this data had not proven to be especially useful. Care was taken to start with metal, which had never been treated with grain refiner, to get away from the problems with the first few runs of the first set.

The Variables

Salt Adsorption Media

The plan was to run only 2 types of filter media. One type was a bed of pellets much like the ones used in the first set of tests. The pore size was increased slightly because that variable seemed to have a positive effect on capture efficiency. The second type of salt filter was a different type of filter plate. This was a very coarse ceramic foam filter made from the salt media composition. It was placed vertically in the trough just up stream from the filter bowl. The top of this filter protruded above the metal. The idea behind this was to allow a means for the air inside the pores of the foam to remain at close to atmospheric pressure in case that would have an effect on adsorption performance.

Ten casts were planned: three with each of the types of salt filter media and three with no media. The tenth cast was to be used to repeat any one of the experiments that might have had problems.

Chlorine Injection

This was held constant at an intermediate level of 6 SCFH.

Ceramic Foam Filter

The conventional ceramic foam filters used for this run were 40 ppi on top and 60 ppi on the bottom. For the first set 30 and 40 ppi filters had been used. The finer filters were used for this run to eliminate as much of the solid inclusions as possible, thus making effects on the salt related inclusions more pronounced.

Testing Procedure

For the first three casts the testing procedure was the same as the first set. That is, the casts were started with no chlorine injection until a LIMCA II baseline was established.
It was then run at 6 SCFM for the remainder of the cast.

For the remaining seven experiments, the chlorine was run for the entire cast.

LIMCA II, LAIS and chill mold samples were taken as before with the exception of not sampling upstream from the degasser.

4.1   Results and Discussion

Results of this set of experiments are summarized in table 4.1.

For the first three casts results were not much different than the previous experiments. However, the response changed dramatically when the chlorine was injected for the entire cast.

Figure 4.2 shows a typical LIMCA II run chart for these experiments. Although the cast would generally begin with high capture efficiency, very high releases of inclusions were seen in the last half of the run.

There was some concern that a mistake had been made in the production of the salt media, either in its formulation or in its heat treatment. To test this idea cast number 774741 was made with salt pellets from the fist set of experiments. Results were much the same, indicating this problem was probably associated with running the chlorine for a longer period of time.

Table 4.1 Raw Data from Second Run – LiMCA, LAIS, and gdms

Drop #	Conditions (1=small; 2=large)				Before Filter			
	Pore	Phys	CFF Filt	Ppm Ca	N20	LAIS	gdms	N20
B1a	none	---	40/60	low	19.23			0.32
B1b	None	---	40/60	low	8.64	0.440		0.16
B2a	3	2	40/60	low	5.29			0.358
B2b	3	2	40/60	low	16.77	0.236		1.02
B3a	2 plates	---	40/60	low	13.1			0.33
B3b	2 plates	---	40/60	low	9.76	0.327		0.53
B4	None	---	40/60	low	46.2	0.140	16	2.59
B5	3	2	40/60	low	15.19	0.586	16	5.77
B6	2 plates	---	40/60	low	12.28	0.787		5.56
B7	None	---	40/60	low	22.3	0.458		3.86
B8	3	2	40/60	low	17.5	0.337	14	7.22
B9	1	2	40/60	low	20.8	---	13	10.4
B10	3	2	40/60	low	16	0.263		8.5

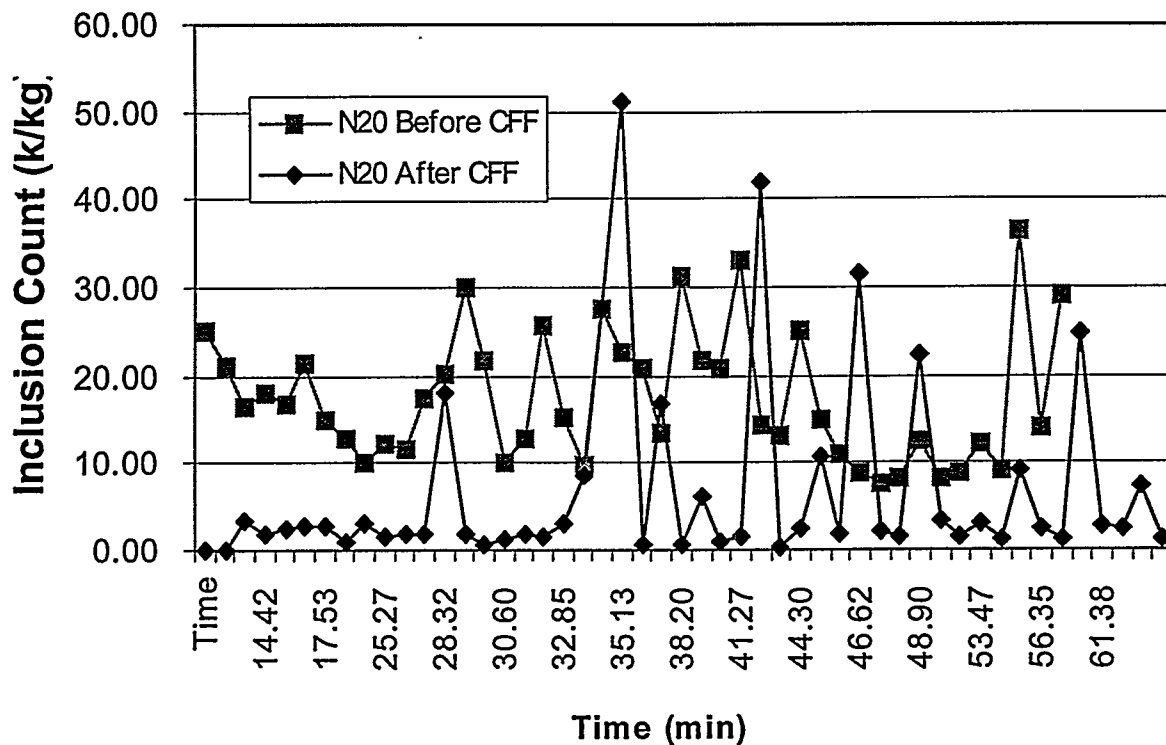"a" at end of drop number indicate first half of the drop
"b" at the end of the drop number indicate the second half of the drop
"1" indicate "small"
"2" indicate "large"
"3" indicate "very large"

Figure 4.2: Typical LiMCA Run Chart Showing Large Releases

Another possible explanation for the inclusion releases in the second half of the run was that the media was reaching its saturation point and could simply hold no more molten salt. This idea was somewhat supported by the observation that dark discoloration associated with salt adsorption was evident all the way to the center of the pellets.

(See Figure 4.3) In the first set of experiments, the discoloration was seen only near the surface.

Figure 4.3: Photograph of Salt Media Showing Complete Reaction of the Pellet
(Second set of experiments)
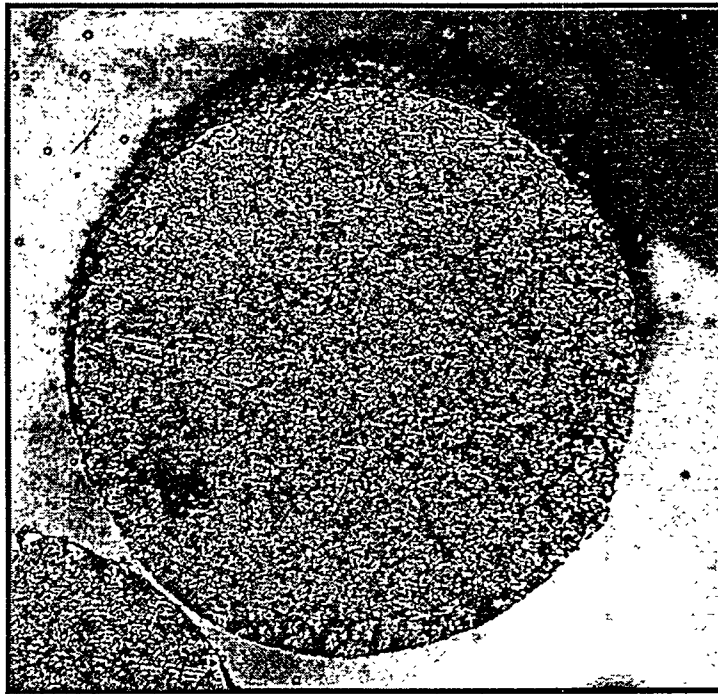
To test this idea the last cast, 774742, was made with an increased quantity of salt adsorption pellets: 10 kg rather than 3 kg. This increase was made possible by using a larger ceramic foam filter in the top of the filter bowl thus creating a larger space between the two ceramic foam filters to pack with salt adsorption media.

The results of this run were worse yet.

In spite of these large releases, the GDMS results indicated a substantial reduction in the chlorine content of the metal when salt media was used.

Subsequent to these runs the LAIS samples were prepared and examined by SEM and EDAX. Figure 4.4 shows a micrograph of a LAIS sample typical of the casts with large releases. The inclusions captured by the LAIS were rich in silica, calcium and magnesium chloride.

Figure 4.4a: Scanning Electron Microscope (SEM) Backscattered Electron Image (BEI) of typical inclusions found in metal after the filter during the casts of the second trial with releases (Cast 774737, Exp. B5)
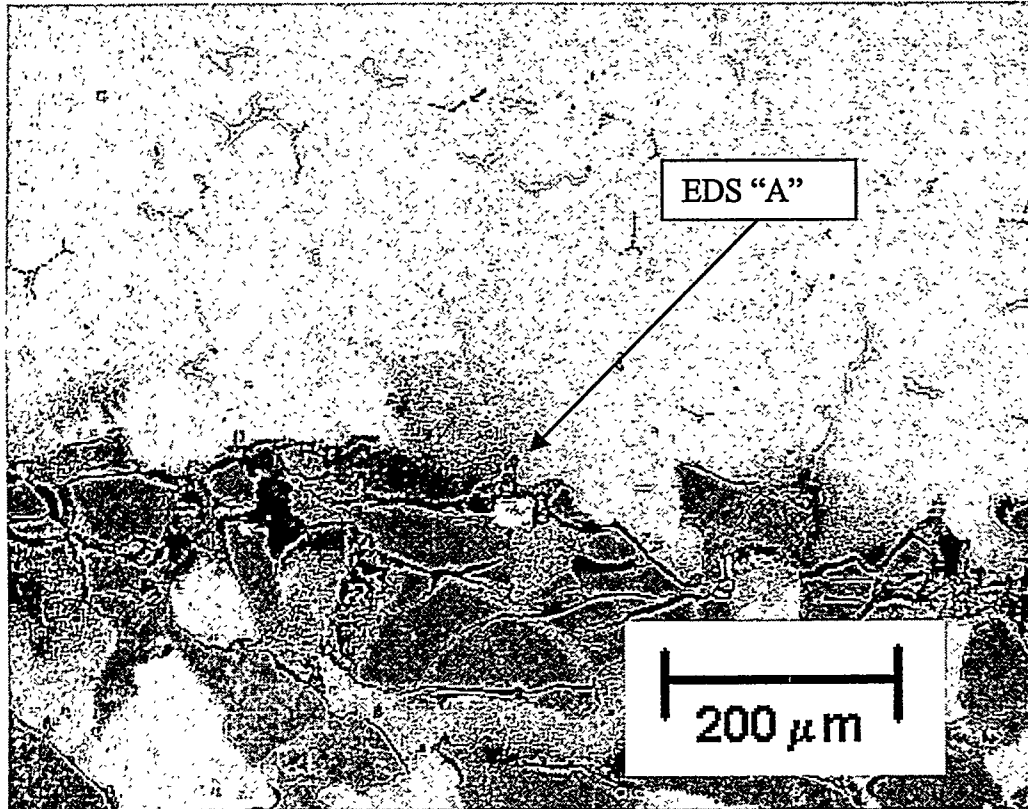

EDS "A"

200 μm

Figure:
SELEE No.:   981047
Sample No.
Image Type:
Magnification: 150

26

Figure 4.4b: Energy Dispersive X-ray analysis of the inclusion marked EDS "A" in figure 4.4a showing the Chlorine peak associated with salts, the Calcium and Silicon peaks originating from the degraded salt media.

H:\REPORTS\DOE\774737\981047SA.spc

Label A:

EDAX ZAF Quantification (Standardless)
Oxides

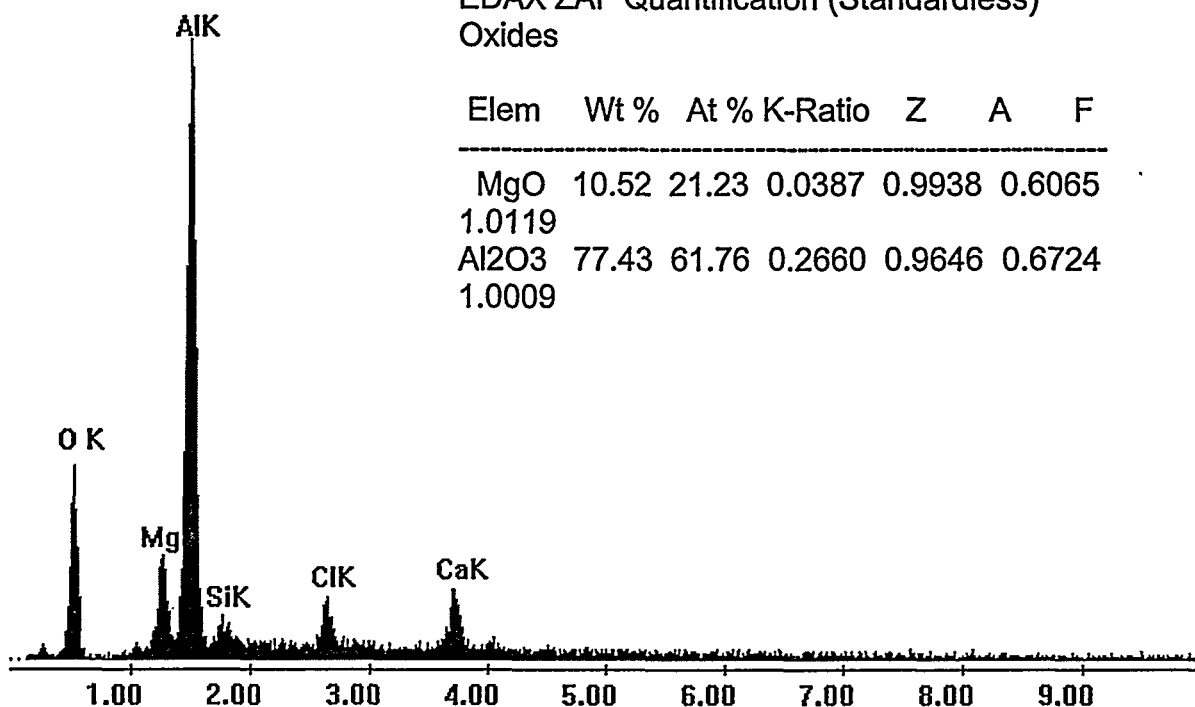| Elem	Wt %	At %	K-Ratio	Z	A	F
MgO	10.52	21.23	0.0387	0.9938	0.6065	1.0119
Al2O3	77.43	61.76	0.2660	0.9646	0.6724	1.0009

Figure:
SELEE No.: 981047
Sample No.
Location: A

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Conclusions and Observations

a) Although the salt media did have the desired effect of adsorbing much of the molten salt it was responsible for large releases of inclusions later in the cast.

b) The composition of the salt media was attacked under these conditions releasing particles high in silica and calcium associated with magnesium chloride.

5.0 Third Set of Experiments

At the conclusion of the second set of experiments it was evident that the formulation of the salt adsorption media would have to be changed to make it more stable.   The laboratory work done to investigate and qualify other formulations was the subject of a separate report, which is attached as Appendix III.

This lab study resulted in two new formulations which appeared be inert to the high magnesium alloys. Of course, in order to function as a salt adsorption media they had to be very porous. The surface had to be wetted by the molten salt, but not by the molten alloys.

5.1 Experimental Strategy

The ten remaining experimental casts were done at the Alcoa Technology Center using the same equipment arrangement as described earlier.   The plan was much the same as the second set of experiments. The two new types of media were to be tested. The plan was for three runs with each type of media, three runs with no media, and the tenth run to be used as needed.

Chlorine injection was either 4 or 5 SCFM and was done for the entire cast.

The finer pore size ceramic foam filters, 40 and 60 ppi were used.

The Salt Media

One of the improved salt media formulations consisted of alpha alumina bonded with a frit that is resistant to wetting and attack by molten aluminum.[3] This is a commercially available material with a softening point of about 1900° F. Enough frit was added to the alpha alumina to cover the grains, thus making the surface non wetting. The frit also acted as a bonding agent for the alumina grain. The alpha alumina itself is ,of course, inert to aluminum alloys.

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The second formulation consisted of a mixture of boehmite and boron nitride. Boron nitride is well known for its very non wetting surface. The boehmite was used as a carrier and a bond for the boron nitride. Upon firing, the boehmite is transformed to gamma alumina, also inert to aluminum alloys.

In both cases the formulation included organic material to form pores. Pellets were extruded and fired.

Results and Discussion

Table 5.1 shows a summary of run condition and results.

It quickly became apparent that the change in formulation had had the desired effect of eliminating the huge releases seen in the second set of experiments. Capture efficiencies looked good according to the LIMCA II results. (A typical run chart is shown in figure 5.2.) The pellets with boron nitride did not perform better than alumina bonded with frit. So the rest of the experiments concentrated on the latter because it is less expensive.

After the first four runs the decision was made to try to change conditions so that the conventional ceramic foam filters without salt adsorption media would have significant releases of inclusions. Previous work suggested that the best way to do this was to increase the flow rate per square inch of filter area. Since the flow rate of the metal could not be significantly increased half the filter area was blocked off. This effectively doubled the flow rate per square inch for the part of the filter that remained unblocked.

Even under these conditions the capture efficiency of the ceramic foam filters alone was high, so the effect of the LIMCA II results was not as dramatic as expected.

On the last day (the last two casts) two additional changes were made, one intentional and one not. The unintentional change was to decrease the amount of argon put into the degasser.

The other change had to do with the LIMCA II data collection. In all previous runs one of the sampling points was up stream of the filter and one down steam. In all cases a probe with an elongated tube was used. This elongated tube is designed to reduce to influence of gaseous and liquid inclusions in the reading. Since liquid inclusions were of primary interest in this study, this was of some concern. The upstream sampling was very close to the degasser so it would not have been practical to use a shorter sampling tube at this point. To get a meaningful direct comparison this meant that the longer tube also had to be used downstream. The magnitude of difference between these two probes was not known. For this reason both LIMCA II units were placed downstream of the filter, one with a long tube and one with a short tube.

In one case there was a 22% difference between the two types of probes and in the other case there was an 8% difference between them.

Table 5.1: Raw Data from Third Experiments.

Cast No.	Salt media	Cl$_2$ (scfh)	Other	Inclusion Concentration after A622 (K/kg)			Inclusion Concentration after Filter (K/kg)			Inclusion Removal Efficiency (%)			LAIS		Ch!
				N20	N50	N100	N20	N50	N100	N20	N50	N100	After A622	After Filter	Aft A6
775547	None	1.5		12.4	0.073	0.000	1.37	0.000	0.000	88.9	100.0	-	0.457	0.039	
775548	BN	1.5		8.99	0.030	0.000	1.15	0.003	0.000	87.2	90.0	-	0.260	0.054	
775549	Al$_2$O$_3$/frit	1.5		11.0	0.069	0.000	1.11	0.002	0.000	89.9	97.1	-	0.374	0.067	
775550	None	2		8.62	0.041	0.000	0.594	0.002	0.000	93.1	95.1	-	0.483	0.059	5.
775551	None	2	1/2 Filter	10.1	0.042	0.000	0.980	0.002	0.000	90.3	95.2	-	0.138	0.035	8.
775552	Al$_2$O$_3$/frit	2	1/2 Filter	9.25	0.032	0.000	0.887	0.000	0.000	90.4	100.0	-	0.318	0.021	8.
775553	Al$_2$O$_3$/frit	2	1/2 Filter	9.69	0.035	0.000	0.479	0.002	0.000	95.1	94.3	-	0.249	0.034	1
775554	None	2	1/2 Filter	7.58	0.015	0.000	0.714	0.005	0.000	90.6	66.7	-	0.234	0.016	5.
775555	Al$_2$O$_3$/frit	5	1/2 Filter	0.262	0.000	0.000	0.203	0.002	0.000	-	-	-	0.079	0.032	4.
775556	None	5	1/2 Filter	0.242	0.000	0.000	0.223	0.000	0.000	-	-	-	0.077	0.027	2

Figure 5.2: Typical LiMCA Run Chart of the New Al₂O₃ & Frit Salt Media Prepared for the Third Set of Experiments (Cast 775552, Experiment C6)
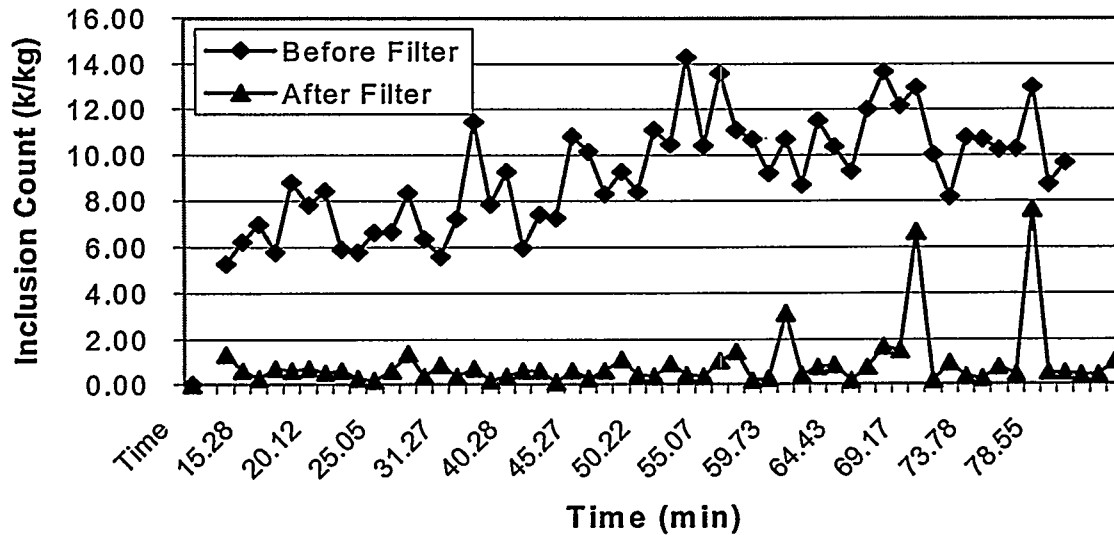
Conclusions and Observations

a) *Under these conditions the performance of the ceramic foam filters was better than anticipated. LIMCA II results downstream of the filters were very low in all cases and no significant reduction was seen comparing runs with salt media to runs without salt media.*

b) *Analysis of the LAIS results showed the same: all metal downstream from the filter was clean, and there was no significant difference between runs with and without the salt media.*

c) *The GDMS showed a very significant difference between the runs with salt adsorption media and the runs without. There was a 42% reduction in chlorine with ceramic foam filters alone while the reduction when salt adsorption media was added was 78%.*

d) *The use of the special elongated probe for the LIMCA II does reduce the detection of salt related inclusions, but this probably was not enough to have much effect on the conclusions of this study.*

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6.0 Salt Probes

In all cases experiments were run with four probes between the degasser and the filter bowl and four probes just down stream from the filter bowl. In the first and second set of experiments one probe was also placed upstream from the degasser. Since the chlorine was injected in the degasser this latter probe was not expected to respond and indeed it did not, even when the same probe was left for several drops.

Probes made for the first set of experiments did not perform consistently. This could have been related to the thickness of the coating, the calcination temperature, the high level of calcium in the metal, or more likely, a combination of these factors.

For the second set of experiments the coating thickness was reduced and the calcium was run at normal levels. Some probes were made with two coats of slurry while another set was made with 3 coats which created coating thicknesses of about 100 and 200µ respectively. The results were much more satisfactory with these probes.

The probes for the third set of experiments were made with 2 coats of slurry and had a median thickness of about 100µ. They also responded as expected.

Probe Response

Figure 1.3 shows a typical positive probe response. Upon immersion the resistance remained high for a period of time and then dropped, usually over a period of several minutes. In several cases the resistance dropped precipitously almost immediately upon immersion. This was taken to be caused by a defective probe; one with a cracked or pitted coating. This was a significant problem for the last two sets of experiments. A total of 22% of the probes were defective in this way. It will probably be necessary to prescreen the probes by dipping them into a crucible of metal to check for conduction. In this way we can eliminate ones that have defects. This also has the effect of leaving a coating of aluminum metal on the outside that could protect the probes during transportation and handling.

It was originally thought that the salt content of the metal could be correlated to some characteristic of the response curve. For instance, attempts were made to correlate the chlorine level to slope of the curve. The time between immersion and full conduction was also considered. Neither of these factors had a high correlation. However, if the probe response is simply considered positive or negative there is a good correlation with the chlorine level as measured by GDMS.

Figure 6.1 is a plot of the probe data from runs 2 and 3. Data from damaged or defective probes as described above were eliminated from this analysis. This plot shows that below about 5 ppm chlorine there was no response. Between 5 and 12 ppm the probes responded sometimes and not others. Above 12 the response was almost universally positive. In the second set of experiments the probes with thicker coating did take longer to respond, but the positive/negative responses were the same.
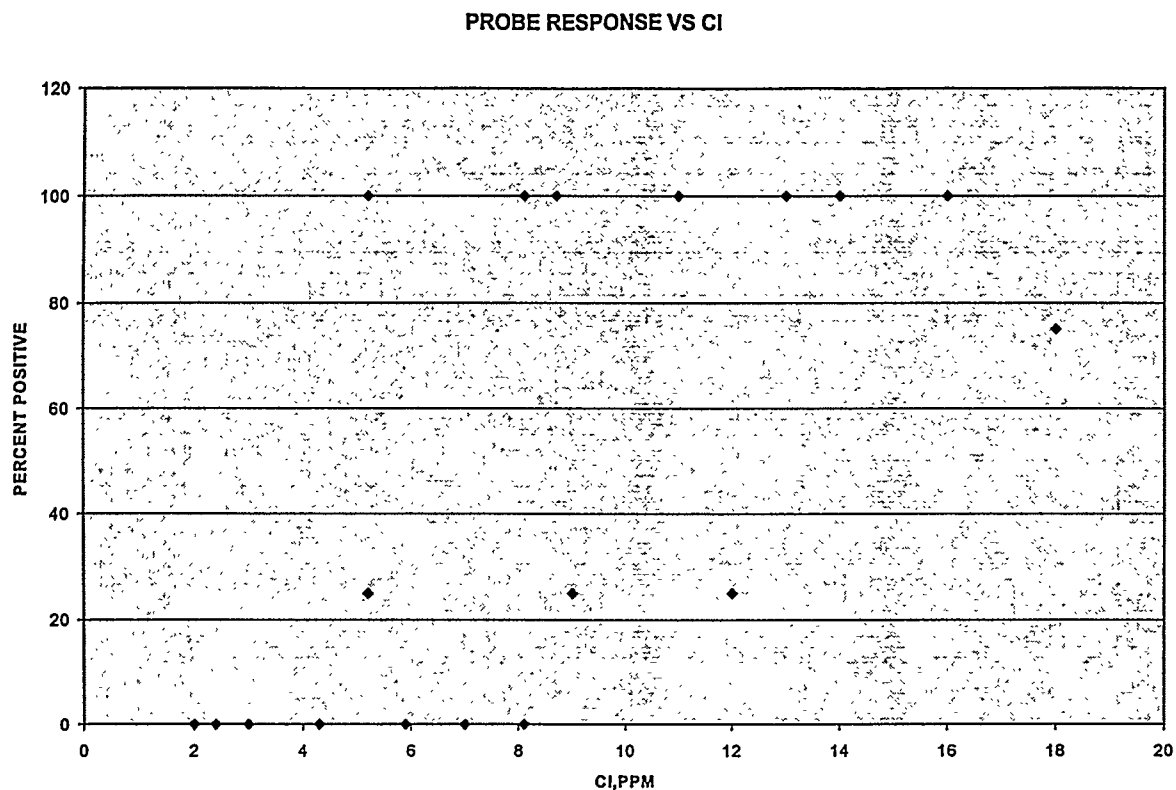
32

Figure 6.1

It may be possible to further refine this response by separating the data on probes upstream from the filter and downstream from the filter. Figures 6.2 and 6.3 show this exercise. It appears that the threshold for a positive response is about 5 ppm up stream and 8 ppm down stream. This may be attributable to the fact that the metal temperature is different in the two locations. For one cast it was measured at 1330 °F upstream from the filter and 1290 °F down stream from the filter.

The liner flow rate will almost certainly be a factor in relating probe response to the concentration of salt in the metal. The flow rate for these experiments was 5.4 ft/min and was not changed throughout the experiments.

UPSTREAM PROBE RESPONSE

Figure 6.2

RESPONSE OF DOWNSTREAM PROBES
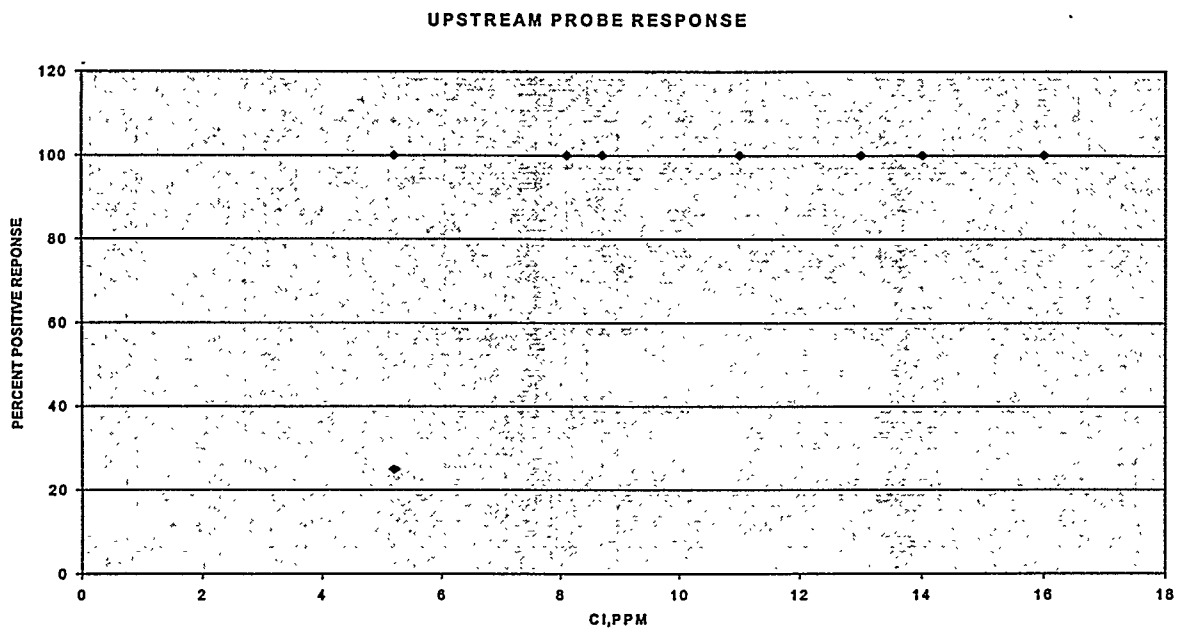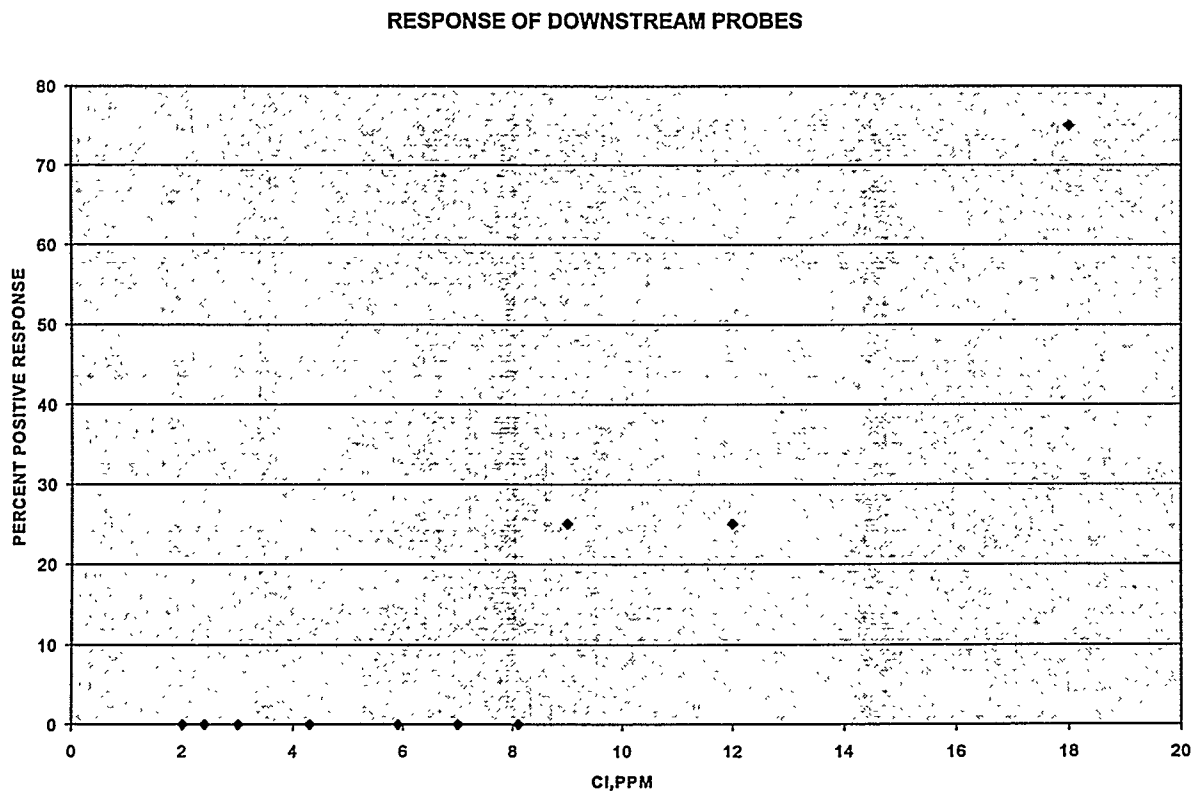
Figure 6.3

Conclusions and Observations

Once the coating thickness was adjusted the probe response correlated well with the chlorine content, a positive response correlating with a minimum chlorine content of 5 to 12 ppm. It may be possible to reduce this range by factoring in metal temperature. This will be studied more in the future.

To eliminate the "false positive "readings due to defective or damaged probe coatings , the probes should be pre-tested in clean metal.

7.0 OVERALL CONCLUSIONS

Use of the salt media consistently improved the removal of salts as measured by the GDMS technique.

In cases where ceramic foam filters of medium pore size (30 and 40 ppi) were used, the result was an improvement in LIMCA II results. In cases where finer pore size ceramic foam filters (40 and 60 ppi) were used the LIMCA II improvement was not significant. Inclusion releases associated with salts do seem to be time related so it is possible that with longer running times the finer pore filters might reach a saturation point, but this point was not reached in the present experiments.

These two conclusions suggest that the LIMCA II does not detect all of the salt present in the metal. This may be because the salt is present in droplets that are outside the size range of the instrument.

A positive probe response correlated to a minimum chlorine level of 5-12 ppm . It may be possible to further refine this resolution by simultaneously monitoring metal temperature.
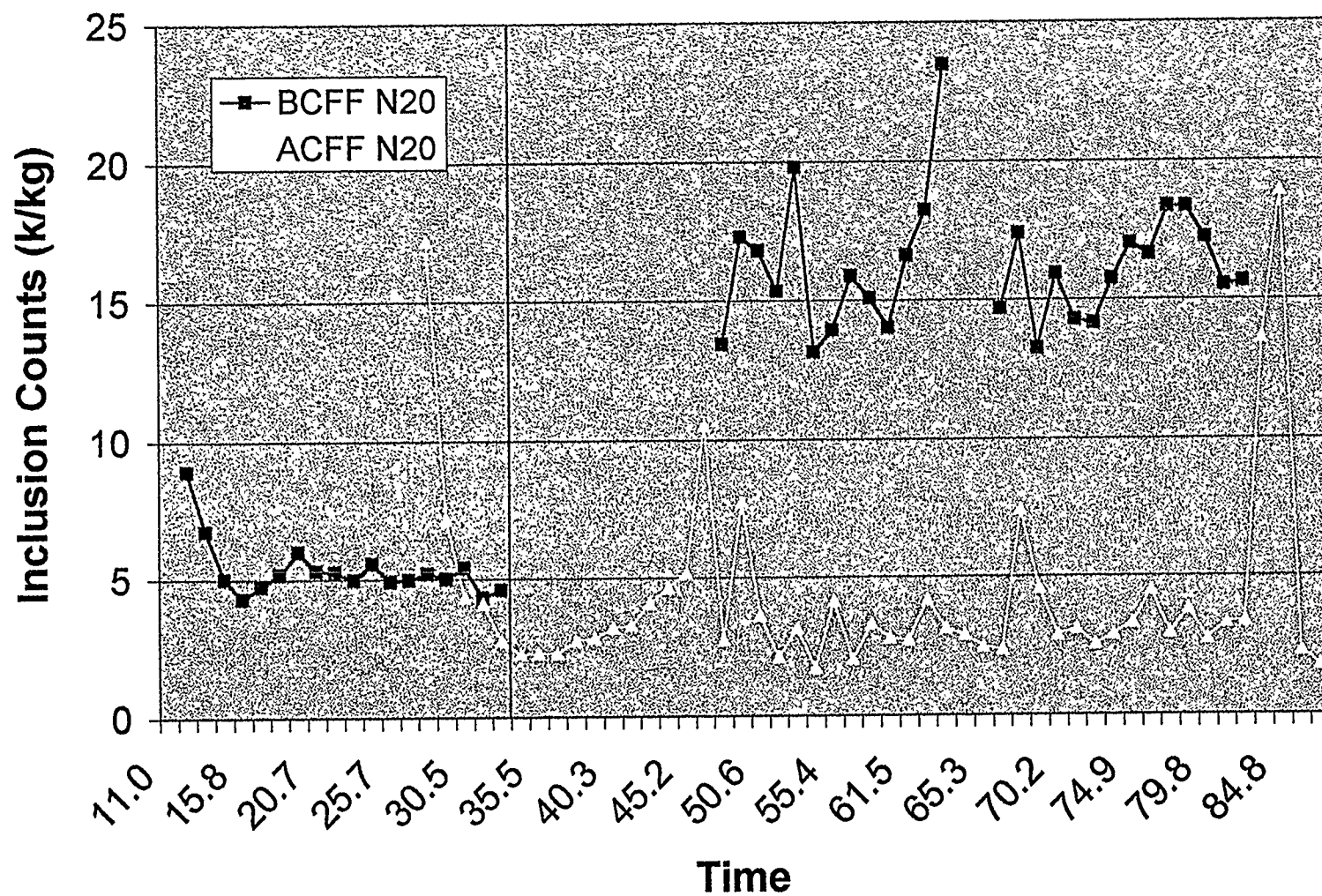
References:

1.   J.A. Eady, D.M. Smith and J.F. Grandfield, "Filtration of Aluminum Melts,"
        ALUMINUM TECHNOLOGY '86, The Institute of Metals, Book 2, Session A, pp
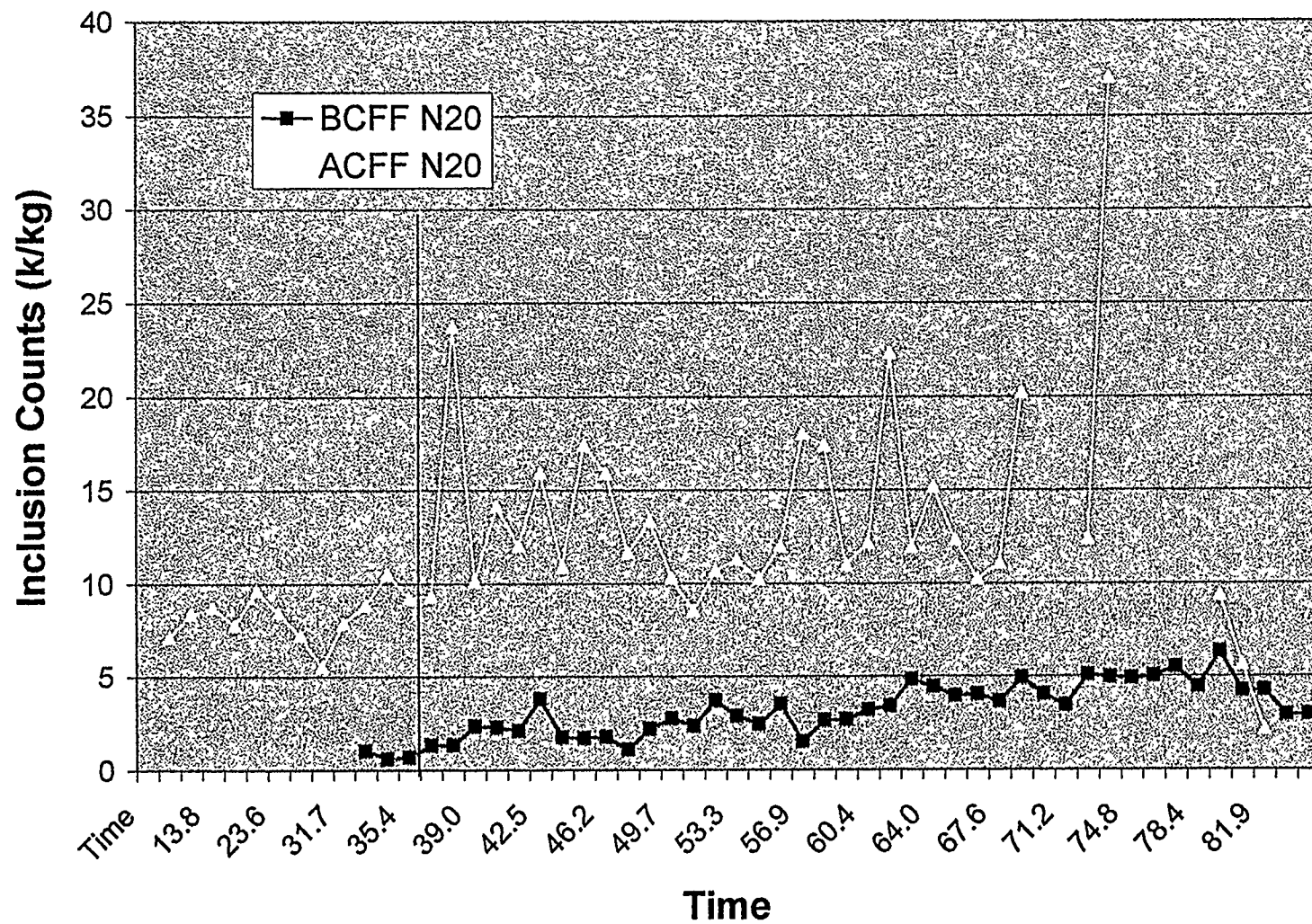   11.11-11.19

APPENDIX I

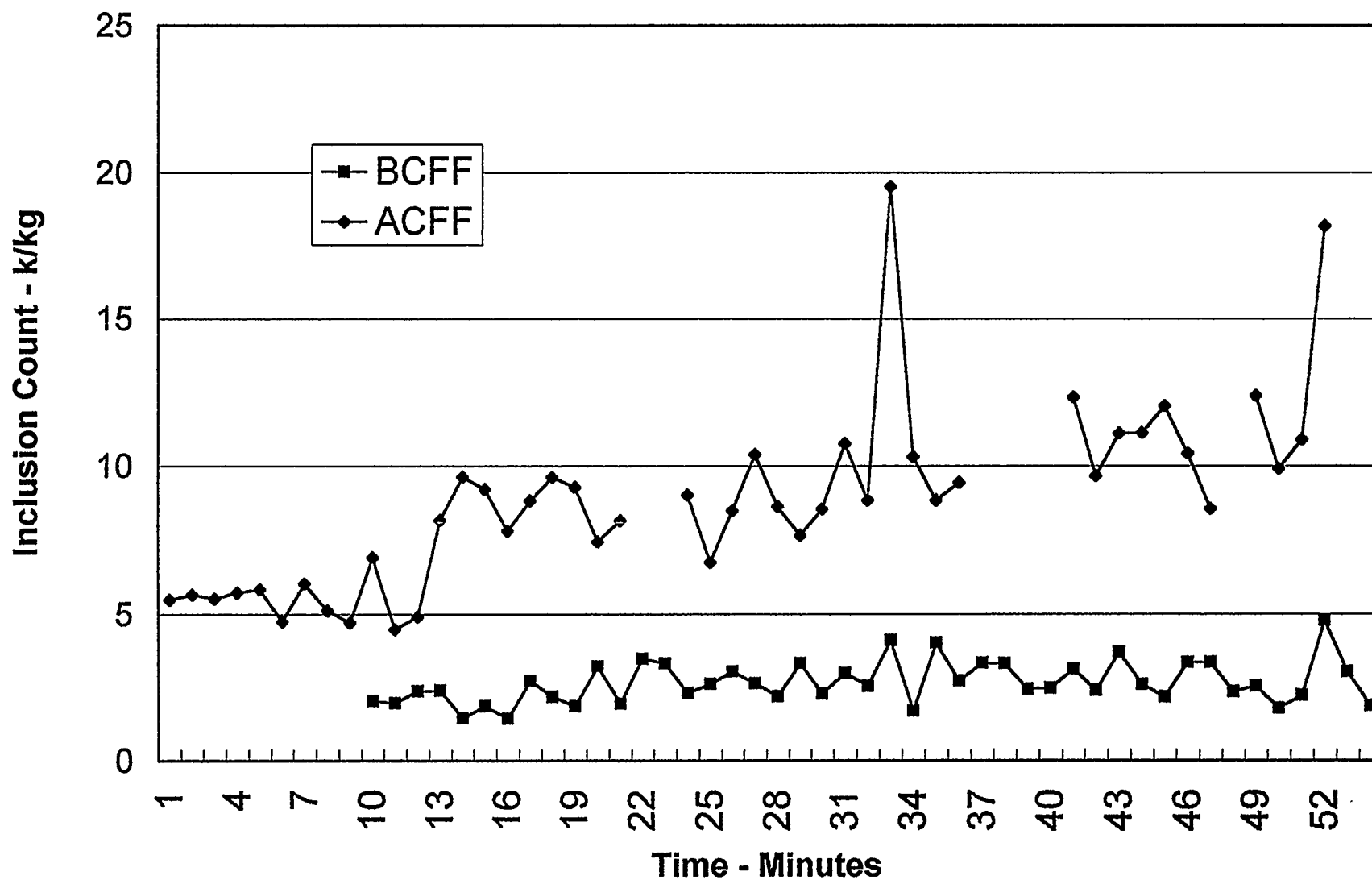**Cast Number 770337, Experiment 13, No Pellets**
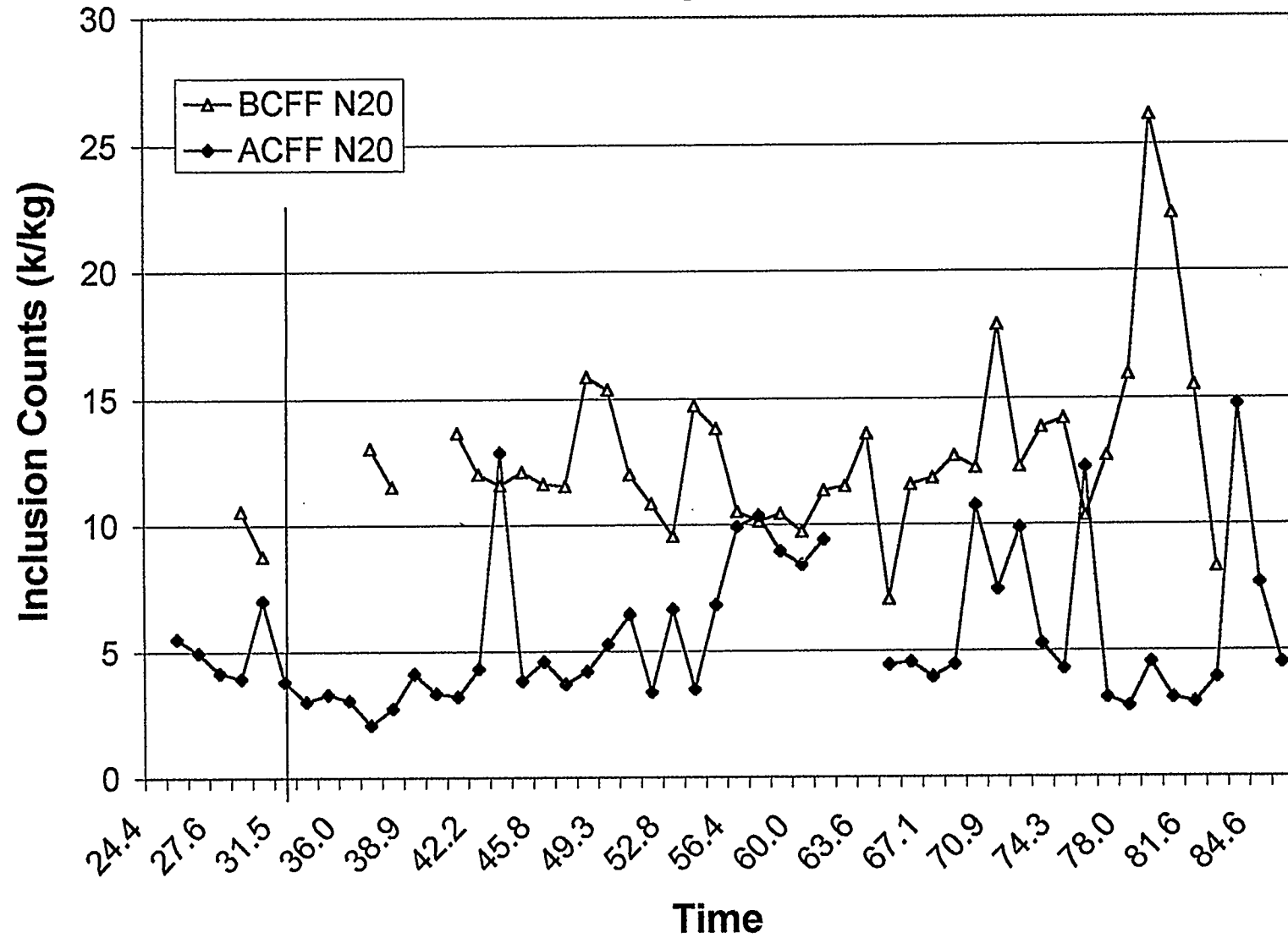
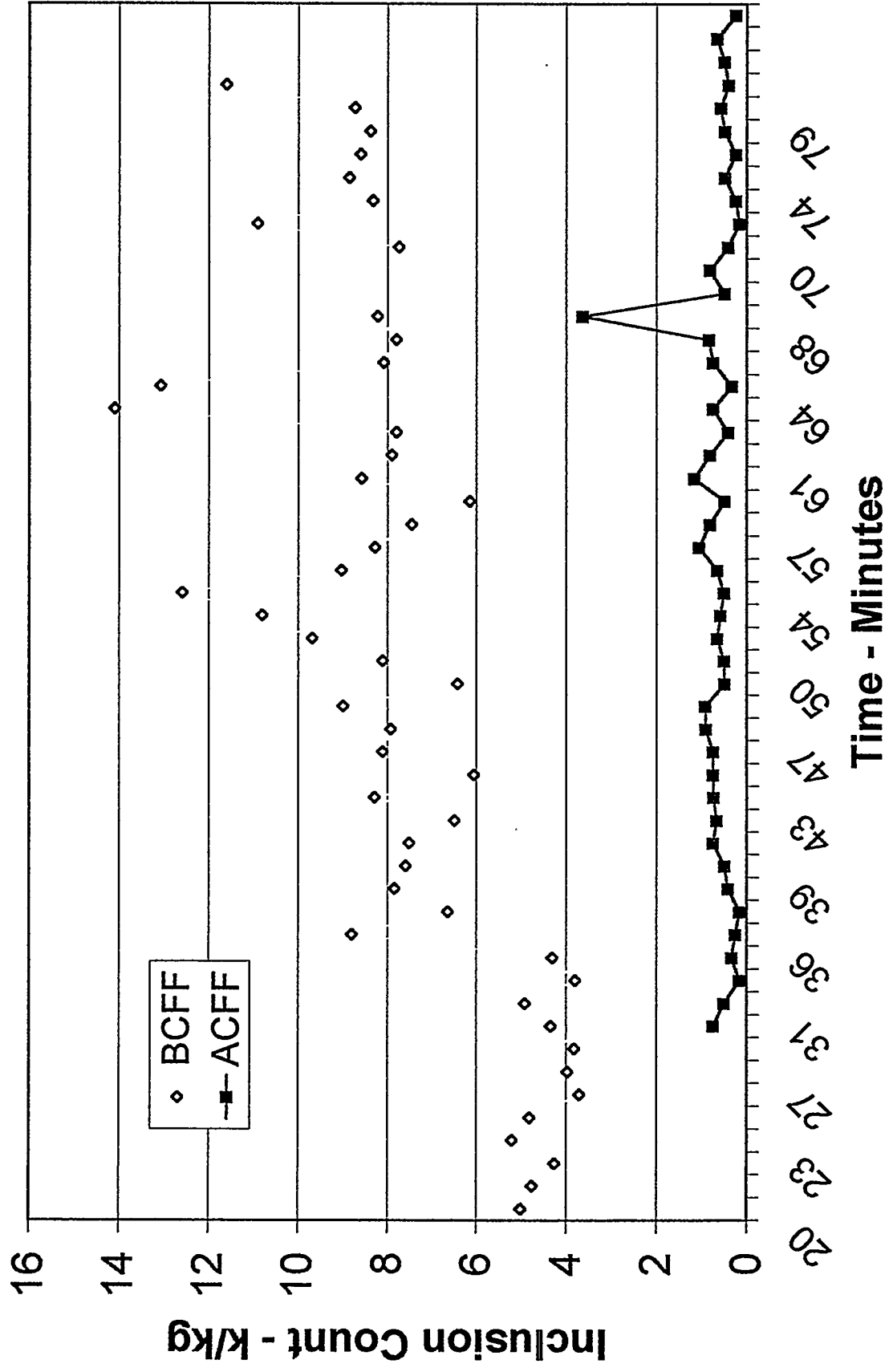**Cast Number 770 338, Experiment 7, Pellet Lot 4A**

Legend:
- BCFF N20
- ACFF N20

Y-axis: Inclusion Counts (k/kg), ranging from 0 to 25

X-axis: Time, values 11.0, 15.8, 20.7, 25.7, 30.5, 35.5, 40.3, 45.2, 50.6, 55.4, 61.5, 65.3, 70.2, 74.9, 79.8, 84.8

Cast Number 770 340, Experiment 14, No Pellets

Cast Number 770 341, Experiment 5, Pellet Lot 4B
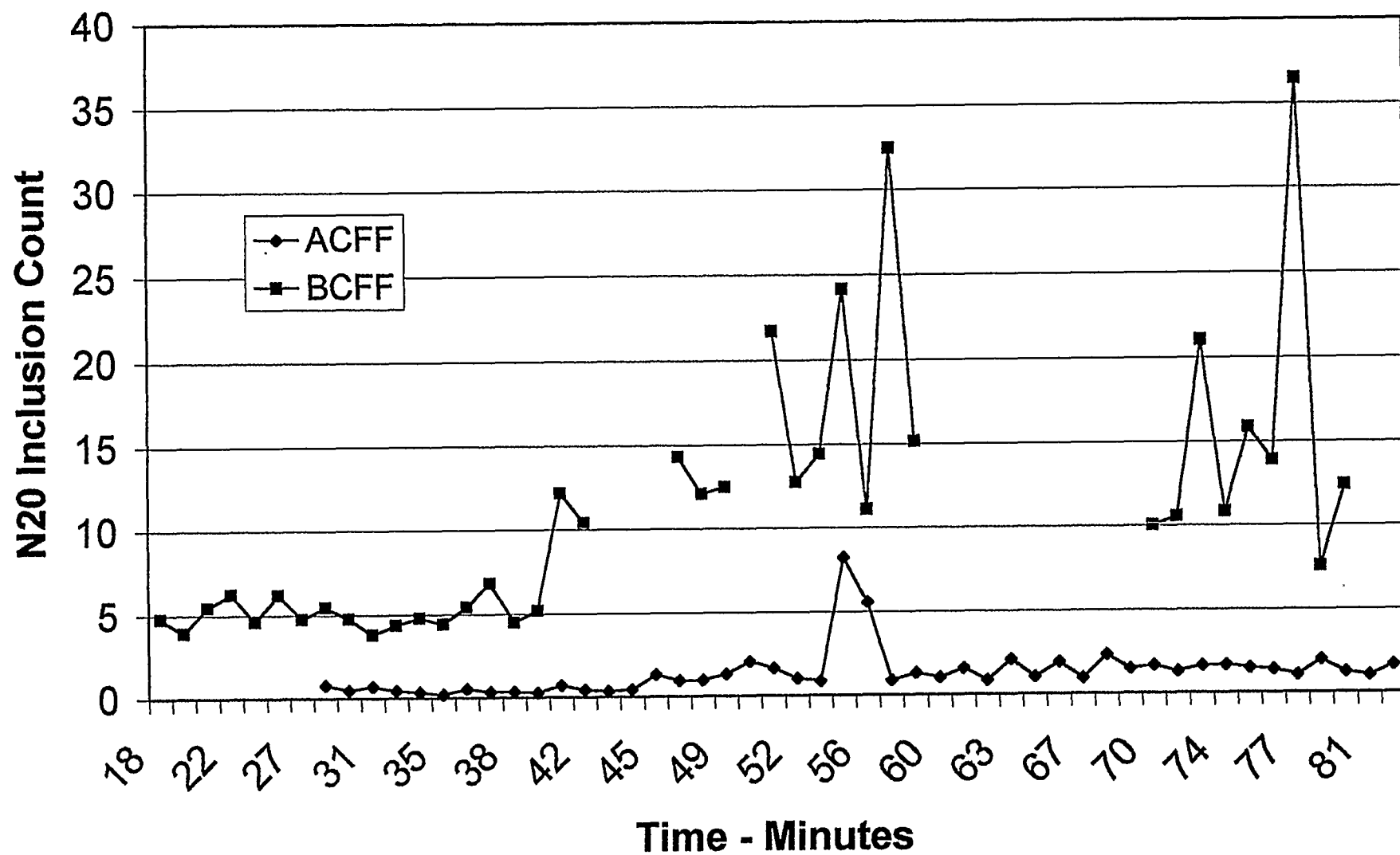
Cast Number 770 342, Experiment 8, Pellet Lot 3A

◇ BCFF
■ ACFF

Inclusion Count - k/kg

Time - Minutes
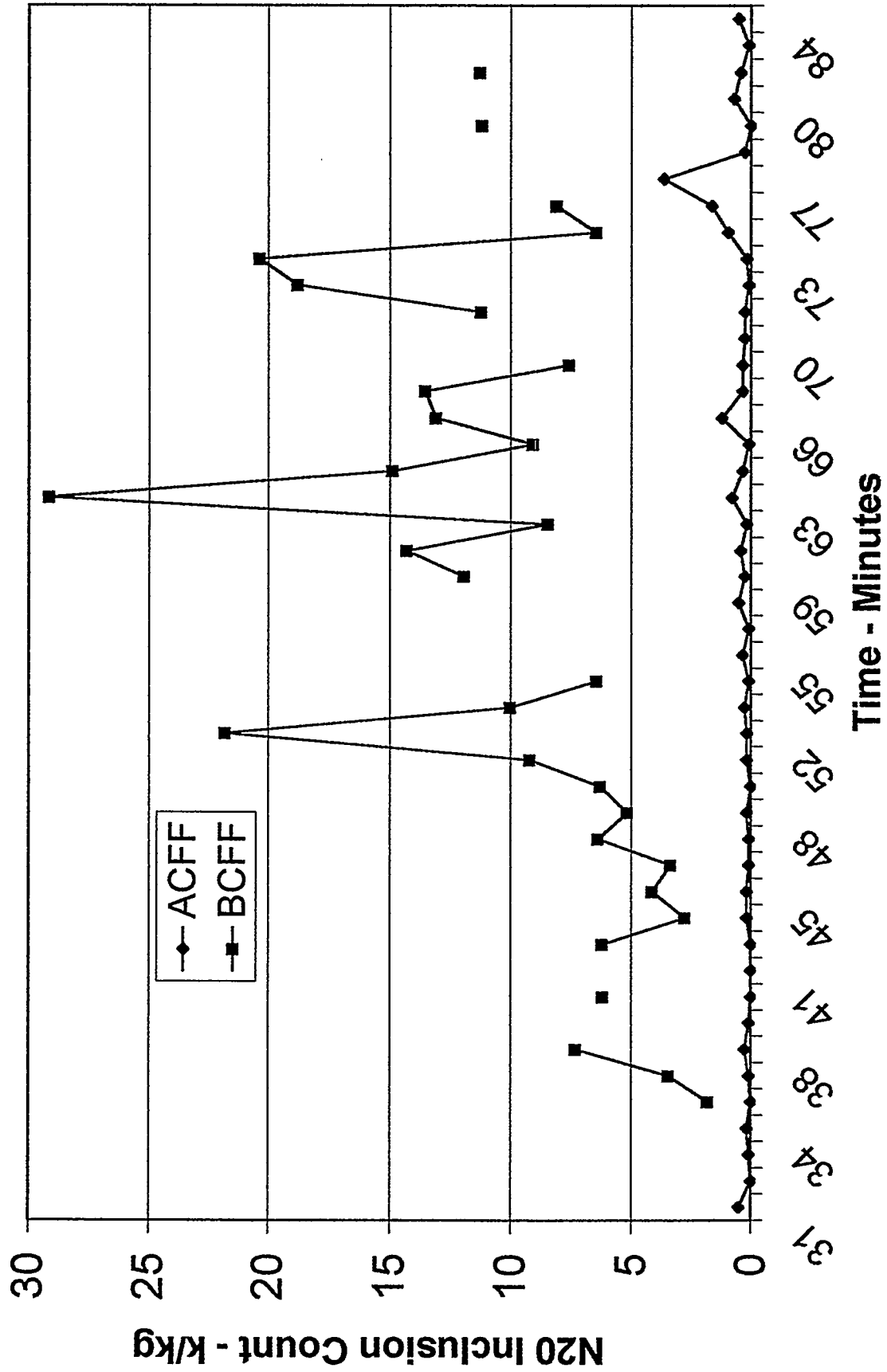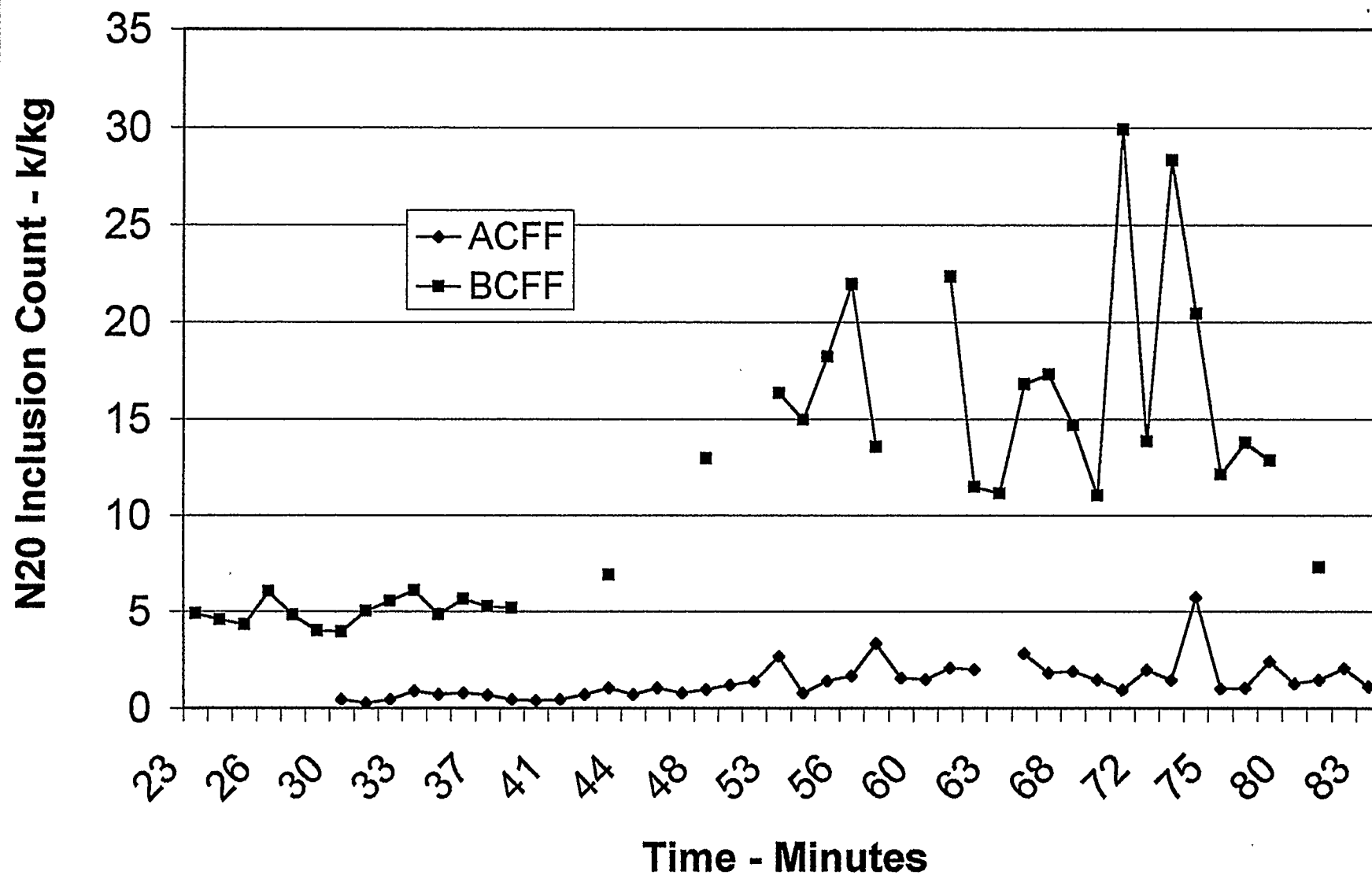
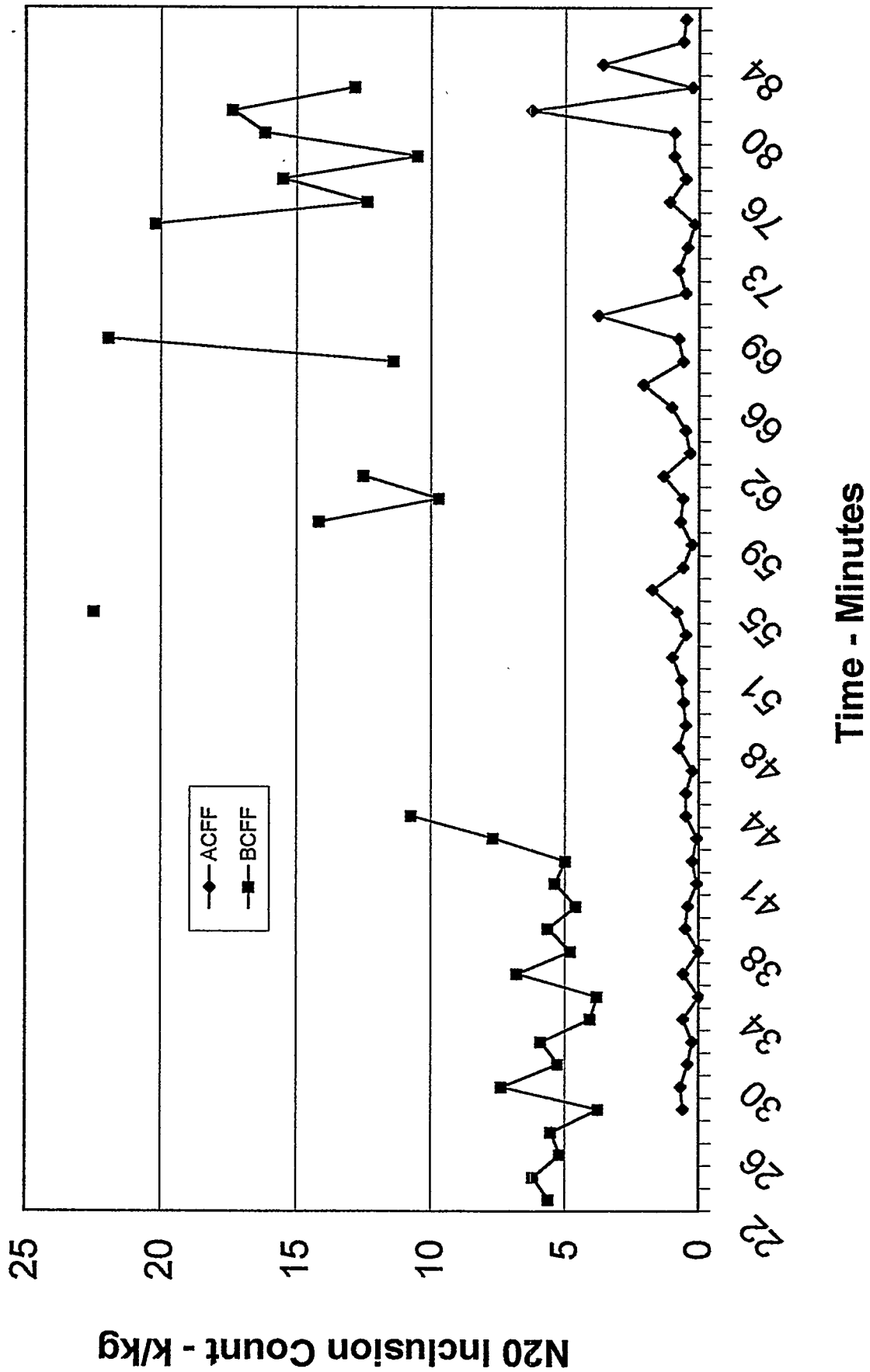Cast 770343, Experiment 9, Pellet Lot 4B
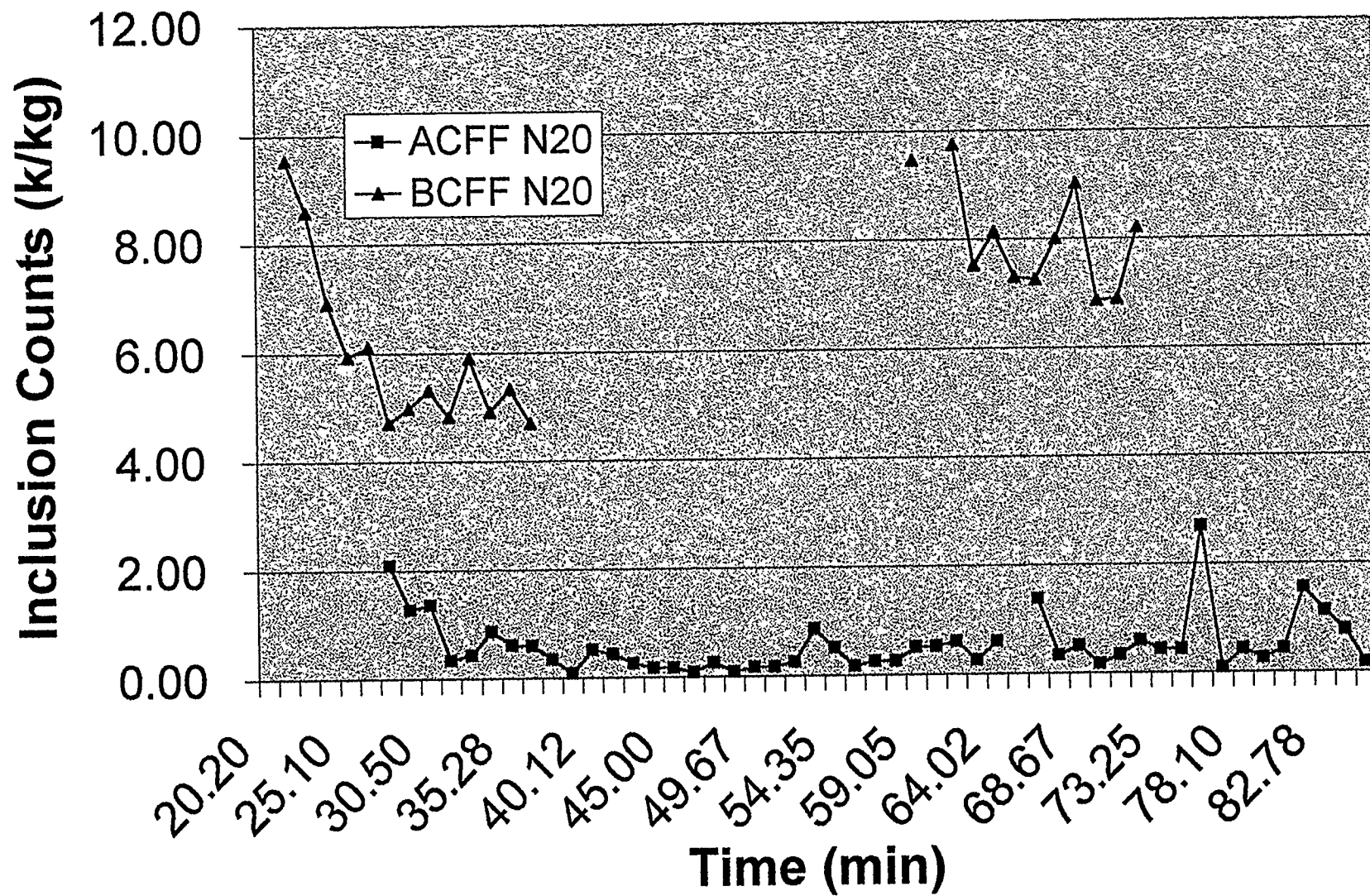
Cast 770344, Experiment 10, Pellet Lot 3B
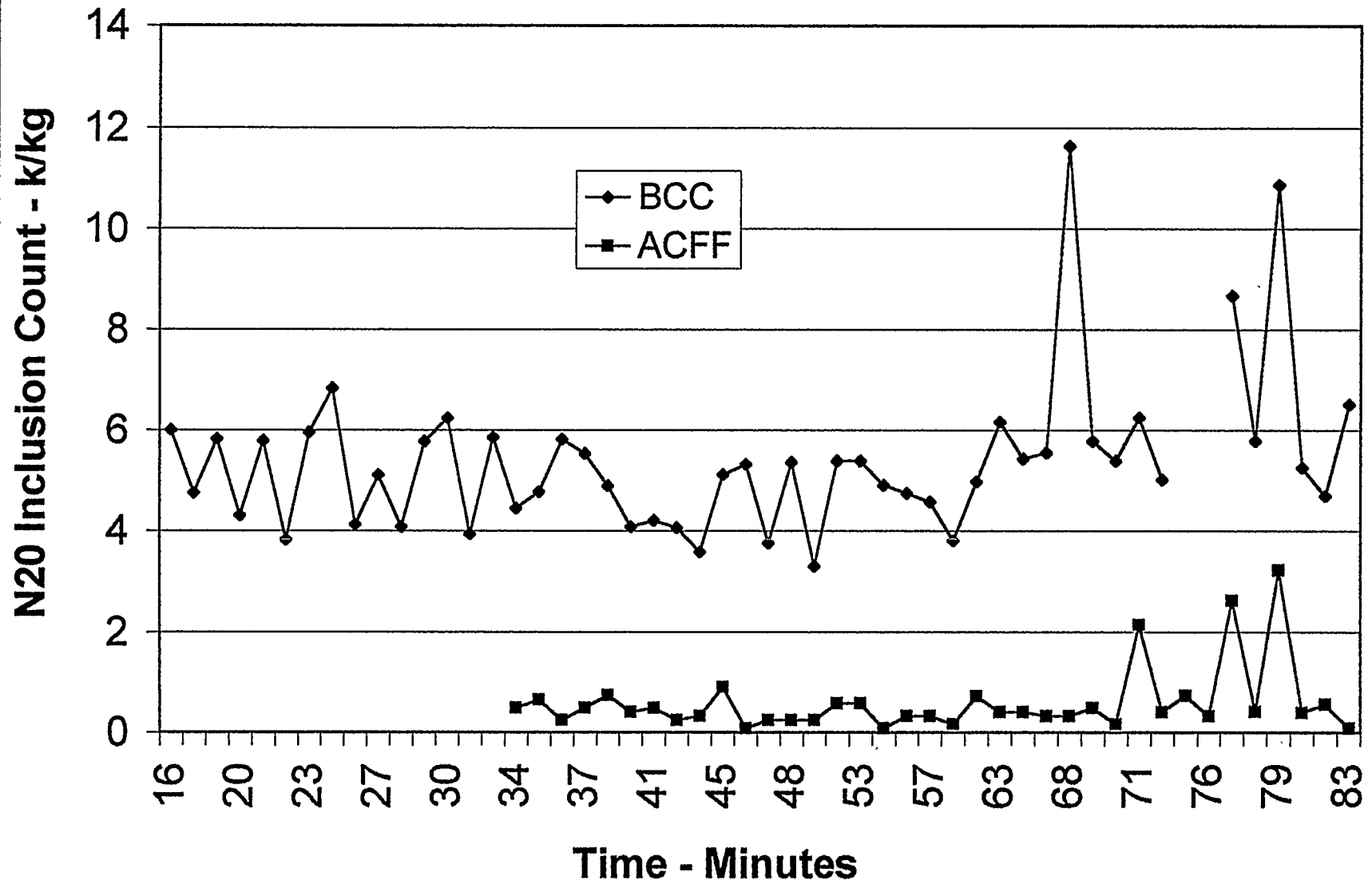
Cast 550345, Experiment 11, Pellet Lot 4A
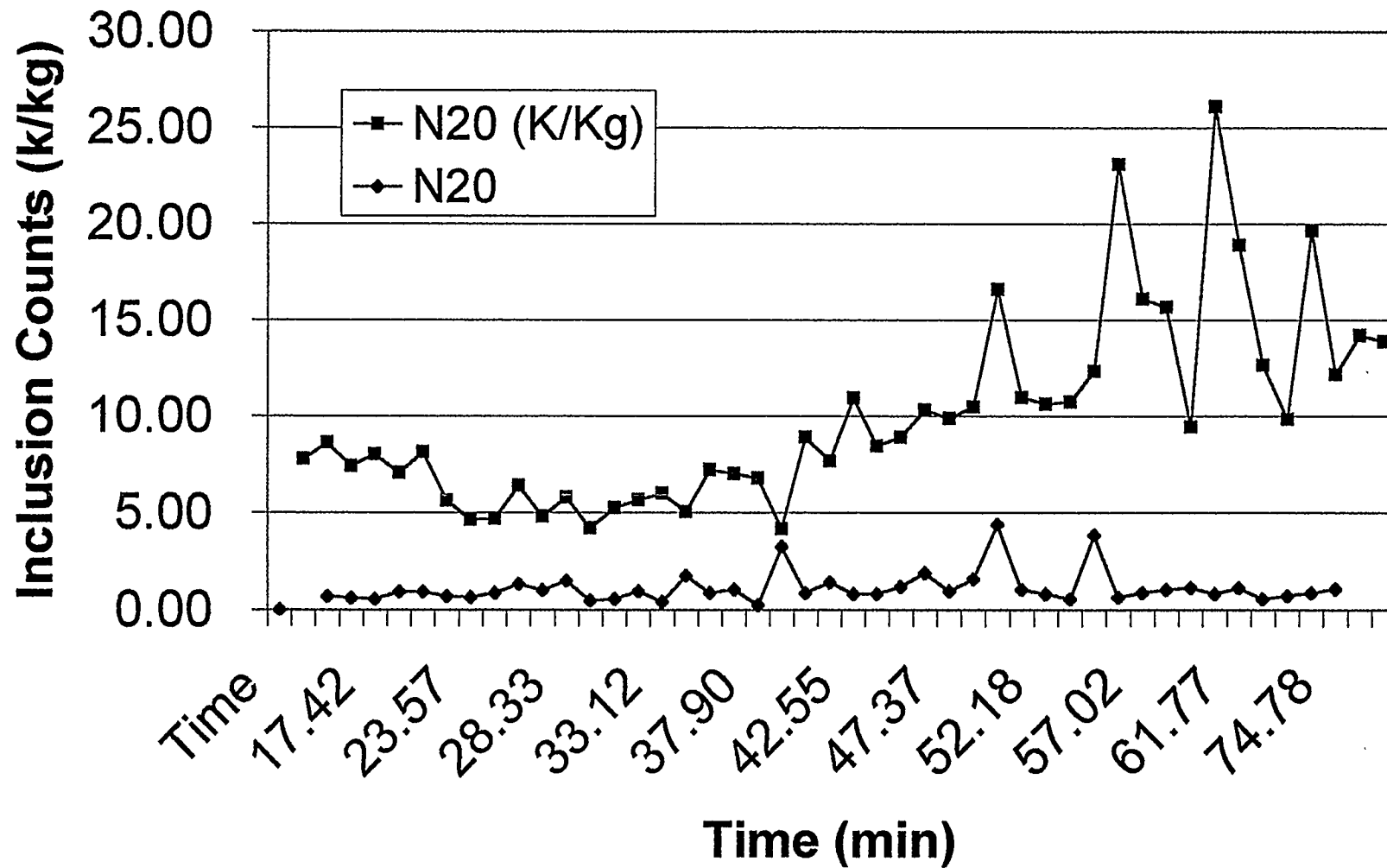
Cast 770 346, Pellet Lot 3A, All Data

Cast Number 770 347, Experiment 6r, Pellet Lot 3B.
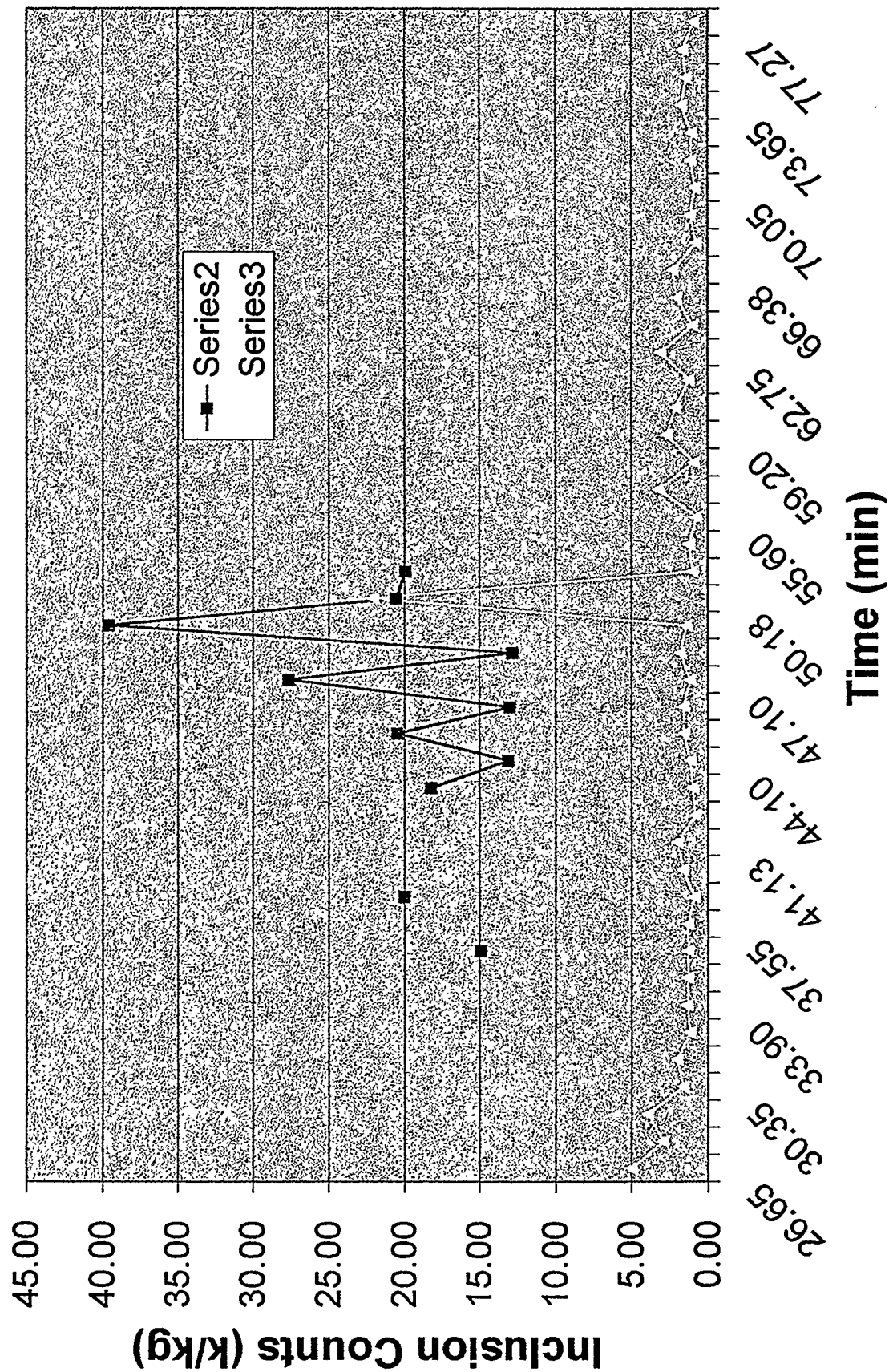
Cast 770349

Cast Number 770351

Cast Number 7770352, No Pellets, Two Filters, All Chlorine

Cast Number 770353, Salt Foam Sandwich, No TiB2

Cast 770 354, 15 PPI Microporous CFF

Cast 770 355, Experiment 20

N20 Inclusion Count - k/kg

Time - Minutes

BCFF
ACFF

Cast 770 356, Experiment 21, TiB2/Low Calcium

N20 Inclusion Count - k/Kg

Time - Minutes

BCFF
ACFF

Cast Number 774733

Cast Number 7747734

Inclusion Counts (k/kg)

Time (min)

Legend: ACFF, BCFF

Y-axis: 45.00, 40.00, 35.00, 30.00, 25.00, 20.00, 15.00, 10.00, 5.00, 0.00

X-axis (Time): 22.15, 27.08, 31.78, 36.55, 41.55, 46.37, 51.07, 55.82, 60.67, 65.50, 70.27, 76.22

Cast Number 7747735

Legend: ACFF, BCFF

Y-axis: Inclusion Counts (k/kg) — 0.00, 5.00, 10.00, 15.00, 20.00, 25.00, 30.00, 35.00

X-axis: Time (min) — Time, 20.28, 23.93, 27.53, 31.13, 34.82, 38.43, 42.10, 45.67, 49.22, 52.73, 56.27, 59.82, 63.47, 67.12, 70.67, 74.22

Cast Number 7774736

Inclusion Count (k/kg)

80.00 70.00 60.00 50.00 40.00 30.00 20.00 10.00 0.00

Legend: ACFF, BCFF

Time (min)

Time 22.58 27.45 32.28 37.10 41.88 47.97 52.75 57.50 62.27 67.07

Cast 774737 (Pellets)

Inclusion Counts (k/kg)

Time (min)

Before
After

Cast 774738 (2 plates)

Cast 7774739: No Pellets

N₂₀ (kJ/kg) vs Time (min)

Legend: BCFF, ACFF

Cast Number 7747740

Inclusion Count (k/kg)

60.00
50.00
40.00
30.00
20.00
10.00
0.00

Time (min)

Time 13.72 18.78 22.37 25.95 29.50 33.07 36.58 40.25 43.92 48.68 52.15 55.72 59.32 62.85 66.35

ACFF
BCFF

Cast Number 7747741

Legend:
- ACFF
- BCFF

Y-axis: Inclusion Counts (k/kg)
Y-axis values: 90.00, 80.00, 70.00, 60.00, 50.00, 40.00, 30.00, 20.00, 10.00, 0.00

X-axis: Time (min)
X-axis values: Time, 22.67, 26.43, 29.97, 33.57, 37.15, 40.77, 44.28, 47.85, 51.40, 54.97, 58.50, 62.05, 65.60, 69.17

Cast Number 7744742

Inclusion Counts (k/kg)

Time (min)

51.40 54.13 56.72 59.18 61.72 64.13 66.58 69.08

ACFF
BCFF

Cast Number 775548

Cast Number 7755549

Inclusion Count (k/kg)

Time (min)

Legend:
- ACFF
- BCFF

Y-axis (Inclusion Count k/kg): 25.00, 20.00, 15.00, 10.00, 5.00, 0.00

X-axis (Time): 19.50, 24.25, 29.07, 33.87, 38.87, 43.77, 48.40, 53.25, 58.07, 62.88, 67.67, 72.52, 77.25

Cast Number 7755550

Legend:
- ACFF
- BCFF

Y-axis: Inclusion Counts (k/kg) — 0.00, 5.00, 10.00, 15.00, 20.00, 25.00

X-axis: Time (min) — Time 17.53, 22.40, 27.30, 32.31, 37.20, 42.25, 47.05, 51.97, 56.78, 61.72, 66.52, 71.32

Cast Number 7755551

Inclusion Counts (k/kg)

Time (min)

BCFF
ACFF
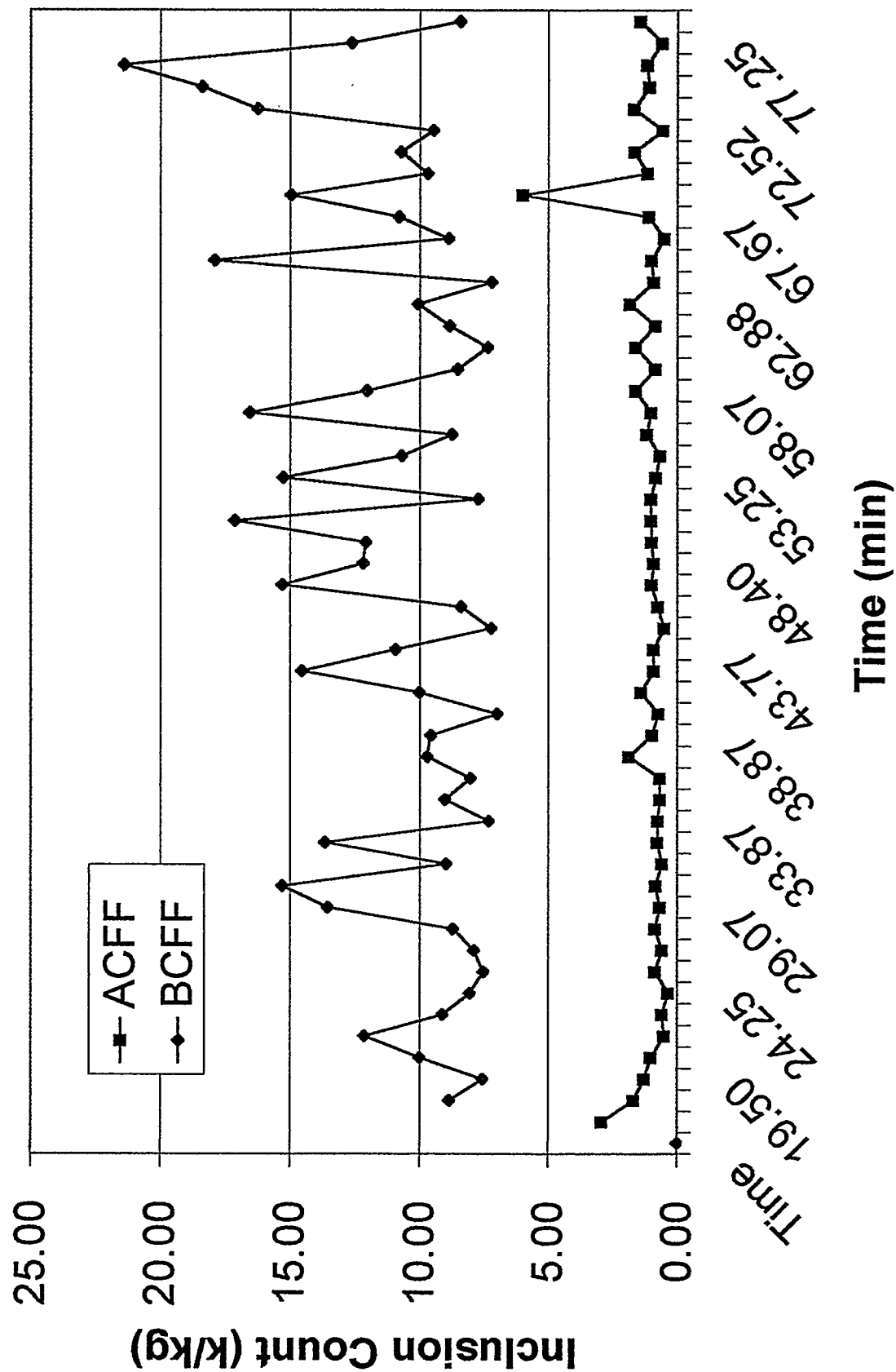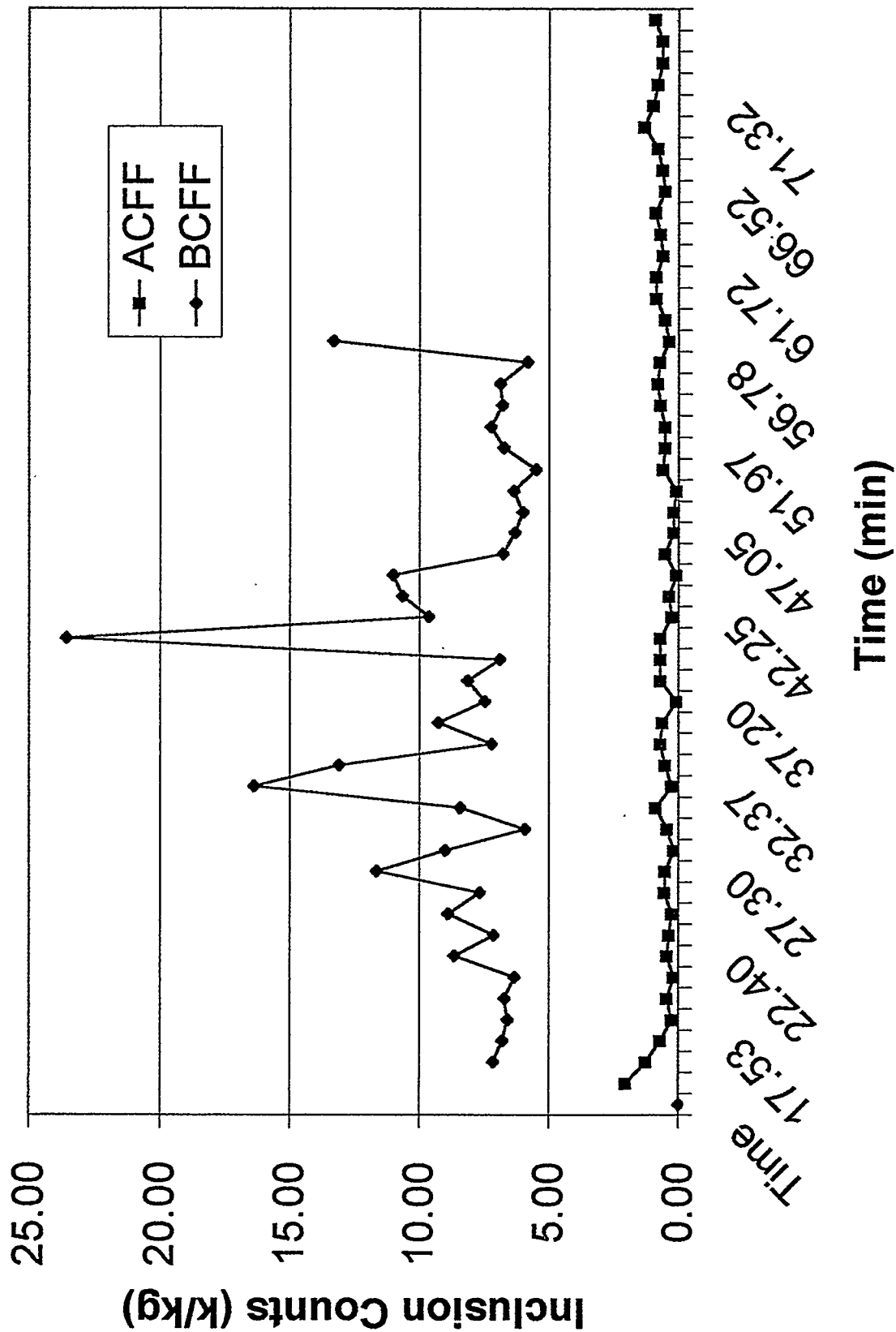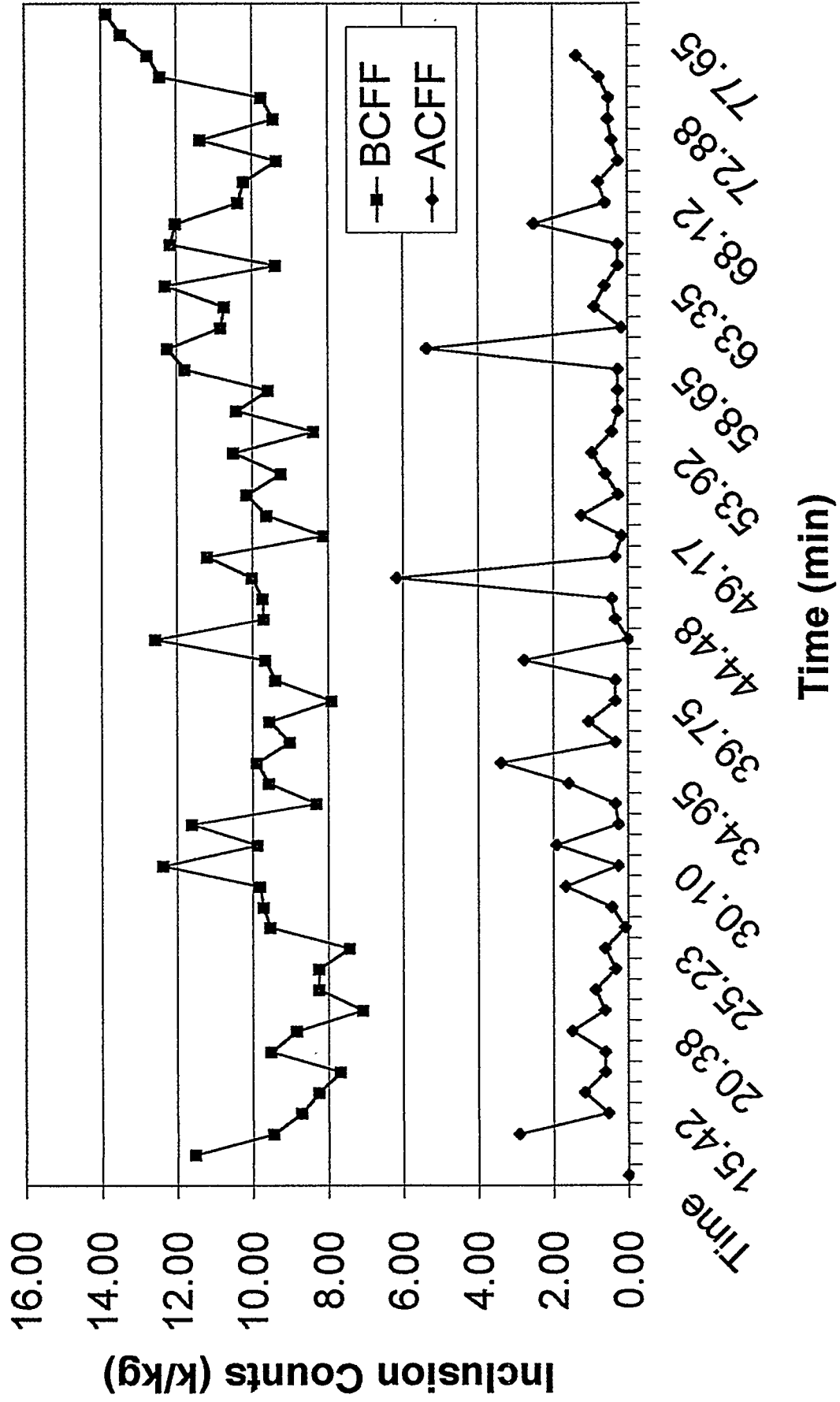
Cast 775552, Exp. C6, Al2O3&Frit

Inclusion Count (k/kg)

16.00 14.00 12.00 10.00 8.00 6.00 4.00 2.00 0.00

— Before Filter
— After Filter

Time

Time 15.28 20.28 25.05 31.27 40.28 45.27 50.22 55.07 59.73 64.43 69.17 73.78 78.55

Cast Number 775553

Y-axis: Inclusion Counts (k/kg)

X-axis: Time (min)

Legend: BCFF, ACFF

Cast Number 7755554

Inclusion Counts (k/kg)

Time (min)

Legend: ACFF, BCFF

14.00 12.00 10.00 8.00 6.00 4.00 2.00 0.00

Time 28.87 32.55 36.10 39.70 43.32 47.02 50.62 54.20 57.83 61.45 65.13 68.80

Cast Number 7755555

Legend: ACFF, ACFF

X-axis: Time (min) — Time 13.58, 18.28, 23.12, 27.93, 32.72, 37.53, 42.37, 47.15, 52.05, 56.88, 61.72, 66.50, 71.30, 76.15

Y-axis: Inclusion Counts (k/kg) — 0.00, 0.20, 0.40, 0.60, 0.80, 1.00, 1.20

Cast Number 7755556

APPENDIX II

Appendix 2: Chemical Analysis of Experimental Casts Made at the Alcoa Technical Center

Cast Number	% Si	% Fe	% Cu	% Mn	% Mg	% Cr	% Ni	% Zn	% Ti	% B	% Be	% Na	% Ca
770 349	0.09	0.21	0.00	0.38	4.54	0.00	0.00	0.02	0.01	0.0001	0.0000	0.0000	0.0041
770 341	0.09	0.20	0.00	0.37	4.66	0.00	0.00	0.02	0.009	0.0002	0.0000	0.0000	0.0047
770 339	0.08	0.19	0.00	0.38	4.52	0.00	0.00	0.01	0.009	0.0003	0.0000	0.0000	0.0039
770 347	0.09	0.21	0.00	0.38	4.16	0.00	0.00	0.02	0.010	0.0001	0.0000	0.0000	0.0021
770 338	0.09	0.21	0.00	0.38	4.49	0.00	0.00	0.02	0.009	0.0002	0.0000	0.0000	0.0021
770 342	0.09	0.20	0.00	0.37	4.66	0.00	0.00	0.02	0.009	0.0002	0.0000	0.0000	0.0047
770 343	0.09	0.20	0.00	0.38	4.56	0.00	0.00	0.01	0.010	0.0002	0.0000	0.0000	0.0028
770 344	0.09	0.20	0.00	0.38	4.56	0.00	0.00	0.01	0.010	0.0002	0.0000	0.0000	0.0028
770 348	0.09	0.21	0.00	0.38	4.16	0.00	0.00	0.02	0.010	0.0001	0.0000	0.0000	0.0021
770 345	0.09	0.21	0.00	0.38	4.49	0.00	0.00	0.02	0.009	0.0002	0.0000	0.0000	0.0021
770 346	0.09	0.21	0.00	0.38	4.49	0.00	0.00	0.02	0.009	0.0002	0.0000	0.0000	0.0021
770 337	0.08	0.19	0.00	0.38	4.14	0.00	0.00	0.01	0.009	0.0003	0.0000	0.0000	0.0031
770 351	0.10	0.21	0.00	0.38	4.62	0.00	0.00	0.02	0.010	0.0001	0.0000	0.0000	0.0037
770 340	0.08	0.19	0.00	0.38	4.52	0.00	0.00	0.01	0.009	0.0003	0.0000	0.0000	0.0039
770 352	0.10	0.21	0.00	0.38	4.62	0.00	0.00	0.02	0.010	0.0001	0.0000	0.0000	0.0037
770 350	0.09	0.21	0.00	0.38	4.54	0.00	0.00	0.02	0.010	0.0001	0.0000	0.0000	0.0041
770 353	0.10	0.21	0.00	0.38	4.77	0.00	0.00	0.02	0.009	0.0002	0.0000	0.0000	0.0017
770 354	0.10	0.21	0.00	0.38	4.77	0.00	0.00	0.02	0.009	0.0002	0.0000	0.0000	0.0017
770 355	0.09	0.22	0.00	0.38	4.59	0.00	0.00	0.01	0.009	0.0002	0.0000	0.0000	0.0006
770 356	0.09	0.22	0.00	0.38	4.59	0.00	0.00	0.01	0.009	0.0002	0.0000	0.0000	0.0006
774 733	0.09	0.13	0.00	0.39	4.63	0.00	0.01	0.00	0.01	0.000	0.0000	0.0001	0.0001
774 735	0.13	0.12	0.00	0.38	4.65	0.00	0.00	0.00	0.01	0.0000	0.0000	0.0006	0.0003
774 737	0.12	0.15	0.00	0.38	4.59	0.00	0.00	0.00	0.01	0.0000	0.0000	0.0001	0.0003
774 739	0.12	0.15	0.00	0.38	4.53	0.00	0.00	0.00	0.01	0.0000	0.0000	0.0000	0.0003
774 741	0.12	0.16	0.00	0.39	4.55	0.00	0.00	0.00	0.01	0.0000	0.0000	0.0000	0.0003
775 547	0.10	0.13	0.00	0.38	4.56	0.00	0.00	0.02	0.006	0.0000	0.0000	0.0000	0.0000
775 549	0.10	0.14	0.02	0.38	4.53	0.00	0.00	0.05	0.01	0.0000	0.0000	0.0000	0.0000
775 553	0.11	0.15	0.02	0.38	4.64	0.00	0.00	0.05	0.01	0.0000	0.0000	0.0000	0.0001
775 554	0.10	0.15	0.02	0.38	4.29	0.00	0.00	0.05	0.01	0.0000	0.0000	0.0000	0.0001

APPENDIX III

LABORATORY EXPERIMENTS ON MODIFIED
SALT ADSORPTION MEDIA

FEBRUARY 5,1999

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A topical report concerning project number: DE FC07 97ID13568

Detection and Removal of Molten Salts from Molten Aluminum
Alloys

1.0 BACKGROUND

As suggested by the title, one intention of this project is to provide a means of removing molten salts from molten aluminum alloys as they are being poured. This is accomplished through the use of a porous ceramic media. The media is made from a material, which is wetted by the salts, but not by the metal. The result is that metal does not penetrate into the pores of the material while the salt is readily adsorbed by capillary action. Thus the media provides a means of separating the two liquids by selective adsorption.

The media used in the first part of this project was made from a mixture of kyanite, several oxides, and one of several organic fillers. This mixture was extruded into pellets (1/8 th or 5/16 inch), then dried and fired. During the firing process the organic fillers were burned away creating a network of pores. The oxides formed a complex boron, calcium, and silica glass that is resistant to attack by molten metal. The kyanite is an inexpensive alumina/silica mineral, which forms the bulk of the body. Although kyanite itself is not resistant to attack by molten aluminum it was believed that it would be completely covered by the protective glass.

2.0 SUMMARY OF FIELD TESTING

To date 30 trial castings have been done at the Alcoa technical center. The results have been reported elsewhere in detail. It appears that the salt adsorption media does indeed remove salt from the metal with an efficiency of about 60-90% depending on specific conditions and which measurement technique is used. However, after long exposure a secondary problem was seen. The LIMCA II, which detects nonmetallic inclusions in the metal stream, showed several releases of high counts of particles. This tended to happen late in the cast.

Two possible explanations were considered:

a) The filter media was simply reaching saturation and then subsequently allowing large amounts of salt to pass.

b) The media itself was breaking down and releasing particles.

In order to determine which of these was happening a trial was done with approximately three times as much salt filter media. If the problem was related to the adsorption capacity of the media the results of this trial should be better. If the media was being attacked it would be worse. The LIMCA II results were, in fact, worse indicating the problem was with the composition of the media itself.

This result was later confirmed by metallography done on spent filter samples.

The overall conclusion was that the concept of using the salt adsorption media was sound, but the media would have to be made more robust for commercial use.

3.0 REFORMULATION OF SALT FILTER MEDIA

The kyanite forming the bulk of the salt filter media is susceptible to attack by the molten metal if not completely covered with glass phase. For this reason it was eliminated in the reformulated pellets. In most cases the kyanite was replaced by alpha alumina. The alumina will clearly be stable in the presence of molten aluminum.

Another possible problem was the glass formation from the oxide mixture. If the oxides do not melt sufficiently and uniformly the glass phase may not have the right composition to be resistant to metal attack. For some of the new experimental pellets the oxide mix was replaced by a frit of the proper composition. The frit was fully melted glass that was milled to a powder. For some of the new pellets the glass phase was eliminated altogether.

Several iterations were made on these principles resulting in three samples that were tested in a laboratory crucible of molten metal:

8A – High fired alumina

8B - Low fired alumina

12B - Low fired alumina bonded with glass frit

4.0 TESTING OF PELLETS

4.1 Salt Adsorption

The first criterion for success was to establish that the pellets were wetted by molten salt. This was done by heating the pellets to about 750 ° C. Particles of magnesium chloride were placed on the surface. In all cases the salt was quickly adsorbed into the porosity of the pellet upon melting.

4.2 Resistance to Molten Aluminum

The second critical criterion for the pellets is that they remain inert to the molten aluminum alloys. In order to effect the selective adsorption of salts, the metal must not penetrate into the pores. Moreover, the pellets must not break down in the metal even when salt is present acting as a flux.

To test the samples described above pellets of each formulation were cemented into holes drilled into an alumina bar. The pellets were heated in a propane flame and magnesium chloride powder spooned onto the surface. The salt was melted and adsorbed into the pellets.

A crucible of a high magnesium aluminum alloy (#5182) was melted and held at 816° C. The alumina bar containing the pellet samples was mounted in a stirring mechanism and immersed into the molten metal. The depth of the samples was 8.5 inches. The stirring mechanism was adjusted to 4 RPM. The samples were left to stir in the molten metal for 4 hours, then removed and allowed to air cool over night.

The conditions described above are more severe than the field test conditions. In the Alcoa cast shop the metal temperature was about 750° C and the duration of the cast was about 1 hour.

4.3 Analysis of Exposed Samples

The samples were sectioned using a water-cooled abrasive saw and mounted for SEM examination. Results and micrographs are shown in the attached metallographic report.

All samples held up well, with no evidence of erosion or metal penetration into the internal porosity.

Sample 12B shows a dark discoloration, which we have learned to expect when the glass frit is exposed to magnesium chloride and metal.

Comparing samples 8A and 8B, the higher fired sample, 8A, appears to be the more inert judging from the smaller amount of adhesion of metal to the surface.

5.0 CONSLUSIONS

High fired alpha alumina and alpha alumina bonded with frit are good candidates for field testing. Elimination of kyanite and nonvitrified oxides should eliminate the release of particles into the metal stream.

Metallurgical Services Analysis

To: **Ken Butcher**
From: **Terri Fisher**
Date: **February 5, 1999**
Re: **Internal – Photos**

Sample preparation

The samples were sectioned, and transverse vacuum mounted in epoxy. The mounted samples were then planar ground and polished. Scanning electron microscopy (SEM) was then performed. Backscatter electron imaging (BEI) was used to differentiate between the metal and inclusion material. Secondary electron imaging (SEI) was used to evaluate the spatial differences in the sample. X-ray energy dispersive spectra (EDS) analysis was used for inclusion quantification.

Analysis

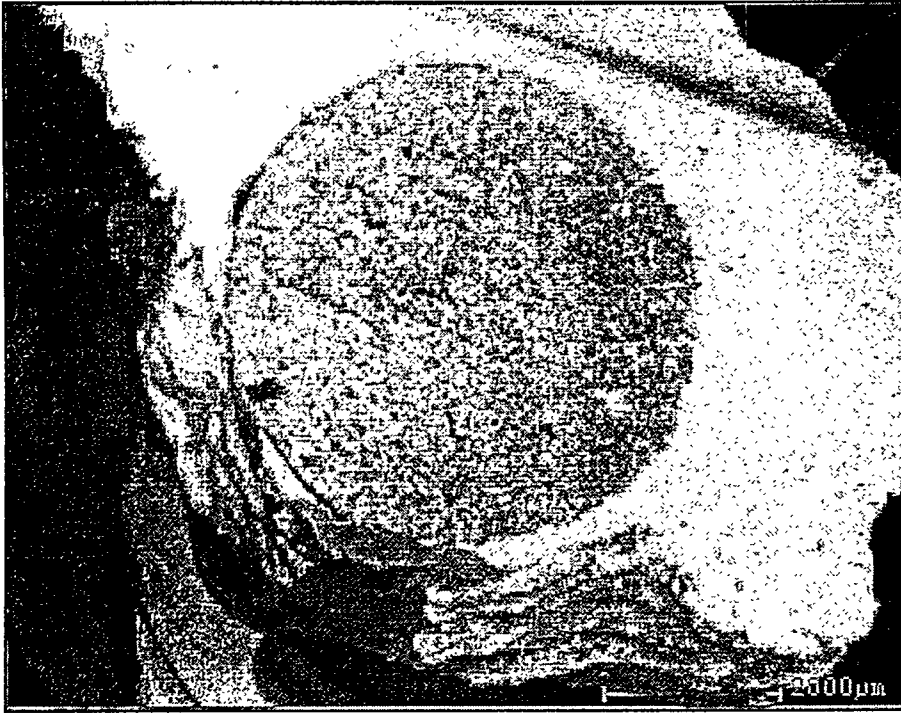The figures showing the results of the SEM analysis are shown below.

FIGURES

Figure 1. SEM/BEI image.

SELEE Sample:8a
Magnification: 12X

Figure 2. SEM/BEI image
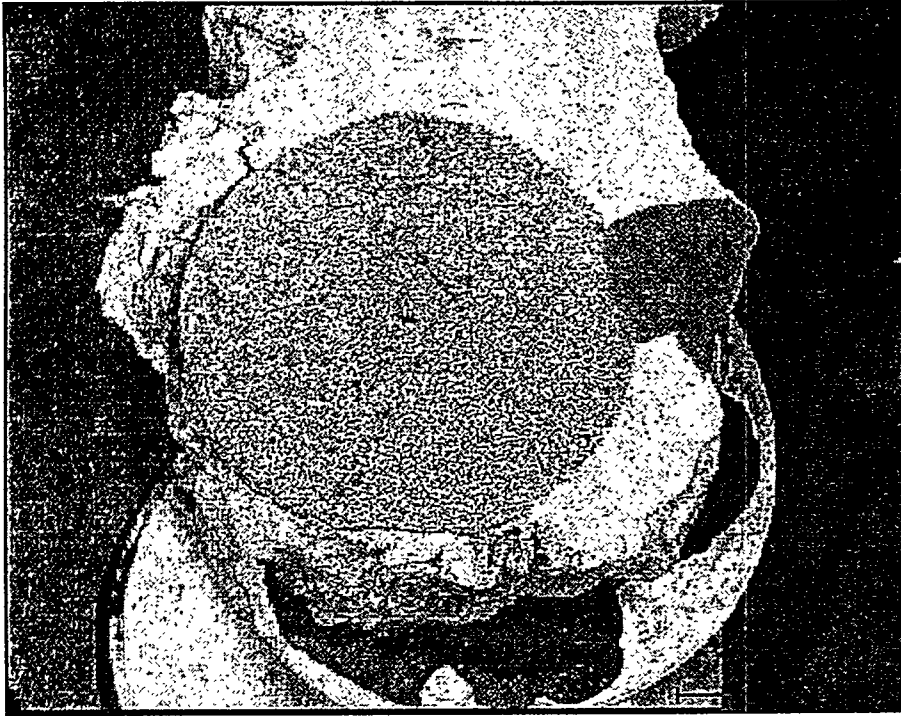
SELEE Sample:8b
Magnification: 10X

Figure 3. SEM/BEI image

SELEE Sample:12b
Magnification:7X

APPENDIX IV

The Role of Reactive Gases on Purging Molten Aluminum

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Abstract

Reactive gases are used when purging molten aluminum to aid hydrogen, alkali and inclusion removal. Chlorine is more effective than fluorine, this fact has been explained as resulting from the formation of liquid $MgCl_2$ salt particles when chlorine is present. However, these liquid salt particles may cause loss of filtration efficiency, formation of a crusty layer on top of liquid metal and generate oxide patches on the surface of cast ingots. Elimination of liquid salt particles downstream of the purging process is required. Liquid salts can be eliminated by limiting the amount of chlorine used, filtering liquid salts or using Cl_2-SF_6 mixtures, as a small addition of SF_6 can remove the liquid salt particles. Careful control of chlorine addition is practiced by several cast shops, others use Cl_2-SF_6 mixtures, no commercial application of liquid salt filtration has been reported thus far.

Introduction

Most aluminum cast in the world today is purged in one or more of several different ways. Pure reactive gases are seldom used nowadays. A solid fluxing agent capable of generating a reactive gas, which was quite common previously, has also become less predominant. Pure inert gases or inert gases with varying amounts of reactive gases are the standard types of purge gases. Purging is a common practice for both production of wrought alloys and for making cast aluminum parts.

There are 3 major factors which require purging molten aluminum.

- Hydrogen Removal

  Hydrogen has a very high solubility in molten aluminum, and a low solubility in the solid metal, as shown in Figure 1.[1]   As a result, the presence of H_2 in molten aluminum leads to the formation of porosity on the solid part.
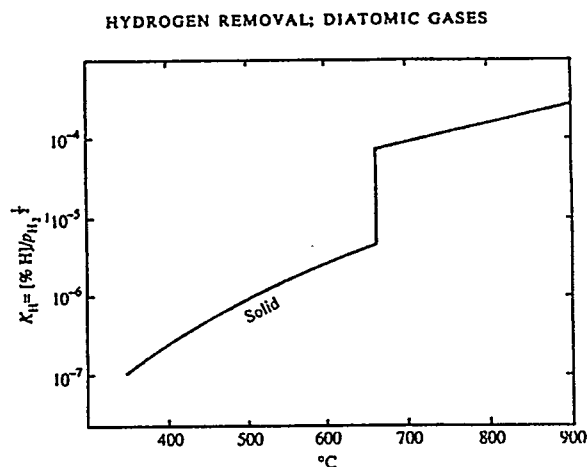
HYDROGEN REMOVAL: DIATOMIC GASES

Figure 1: Solubility of hydrogen (at one bar pressure) in pure aluminum as a function of temperature.[1]

- Alkali Removal

  Sodium, calcium and lithium are often present in molten aluminum. These elements are incorporated into the metal either in the Hall-Heroult electrolytic cell when making primary metal, or from scrap sources when dealing with secondary aluminum. These contaminants can cause defects mainly when fabricating aluminum sheet.

- Inclusion Removal

  Inclusions are generated during the processing of molten aluminum, and may be incorporated in the final product. Oxides, spinels, borides clus-

ters and liquid salts are typical inclusions found in-molten aluminum. Inclusions may cause fabrication defects and negatively affect mechanical properties.

Purging Methods

Three basic methods are used to purge molten aluminum: wands, porous plugs and rotary impeller degassers. The efficacy of these processes to remove hydrogen has been discussed in detail in the literature, and has been well documented as shown in Figure 2.[1]
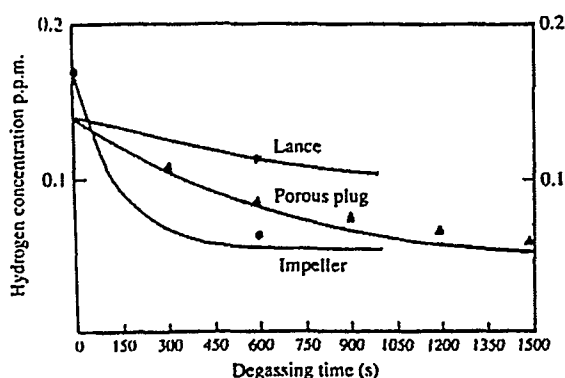

Figure 2: Results obtained with three different degassing techniques in a 500 lb. furnace.[1]

These three methods can be applied in the furnace itself, on an in-line treatment unit, or in a transfer ladle.

The lower efficiency of wands and porous plugs to remove hydrogen is related to the gas bubbles size, as extensively discussed by Sigworth and Engh.[2] Molten aluminum has physical properties similar to water but for surface tension. The surface tension of molten aluminum is very high. In order to generate small bubbles with large specific surface area, a mechanical method of imparting energy such as a rotary impeller degasser is needed. The large gas bubbles formed with wands or porous plugs have low efficiency to remove hydrogen from the metal.

The low hydrogen removal efficiency when purging with wands or porous plugs led to the use of reactive gas for purging of molten aluminum. The use of halogen gases such as chlorine can aid the removal of hydrogen by chemically striping hydrogen from the metal.

Purging Gas Composition

Several purging gas compositions have been used to purge molten aluminum. Pure chlorine gas was extensively used in the past. The high chemical reactivity of pure chlorine aided hydrogen removal. However, the use of pure Cl_2 with wands or porous plugs is a pollution hazard. Large amount of reactive gases are liberated during purging.[3] Commercial purity chlorine is also extremely corrosive. Construction and maintenance of gas handling systems to deliver the chlorine for purging is cumbersome and expensive.

Pure inert gases are sometimes used to purge molten aluminum. Argon is frequently used by wrought alloy producers, nitrogen is used by a number of aluminum foundries. Inert gases can remove hydrogen well when used in a rotary impeller degasser. However, efficiency is lower than reactive gases when used with wands or porous plugs. Also, inert gases by themselves do not remove alkalis and inclusions.

The combination of a inert gas and one or more reactive gases is the most common choice for purge gas currently. The inert gas is either N_2 or Ar as discussed above. The reactive gases are halogens most of the time, four different types of reactive gases will be discussed here.

Chlorine is still the choice reactive gas for purging molten aluminum. It is extremely effective for the removal of hydrogen, alkalis and inclusions. Two practical problems are associated with the use of chlorine. Chlorine handling systems are expensive and complicated, due to its corrosive nature. Also the storage of large amounts of chlorine is a pollution hazard.

Chlorofluorinated hydrocarbons such as FREON® were used as a reactive gas. Dore et.al.[3] describes one possible method of using these gases together with an inert gas. The use of FREON® was quite common mainly in aluminum foundries until the 80's. At that time, FREON® availability became very limited due to the long term effect of that gas on the ozone layer, the use of FREON® for purging molten aluminum diminished considerably.

Sulfur hexafluoride was introduced in the late 80's as a reactive gas for purging molten aluminum.[4] The use of SF_6 has become quite common over the last few years. Several authors have compared the effectiveness of sulfur hexafluoride and chlorine as a reactive gas, chlorine is considered more effective than SF_6.[5] SF_6 has a major advantages that it does not have the corrosion and pollution hazards associated with chlorine.

The use of pure chlorine as a reactive gas has two additional disadvantages. Most aluminum alloys contain magnesium, which leads to the formation of liquid magnesium chloride particles in the melt. These liquid salts can lead to the formation of oxide patches in sheet ingots.[5] Also, liquid salts can lower considerably filtration efficiency.[6] The use of Cl_2-SF_6 mixtures was proposed as a method to eliminate these liquid salts, while still maintaining the high efficiency associated with chlorine.[5]

The Role of Reactive Gases

As discussed above, there are three objectives when purging molten aluminum: hydrogen removal, alkali removal and inclusion removal. Also, the formation of liquid salts during purging with reactive gases is an important mechanism, with both beneficial and detrimental effects. The role of reactive gases on these four processes will be considered

- Hydrogen Removal

    The role of reactive gases on hydrogen removal is strongly related to the purging method. If a rotary degasser is used for purging, the reactive gases do not accelerate hydrogen removal. This is explained in great detail by Sigworth and Engh.[2] The presence of a large number of small gas bubbles well dispersed in the bath can remove hydrogen at a high rate regardless of purging gas composition.

    Purging with wands or porous plugs have a low hydrogen removal efficiency. In this case, the presence of reactive gases can increase the hydrogen removal rate. The actual mechanism is controversial, the following have been considered.

    - The presence of liquid $MgCl_2$ particles aid H_2 removal by improving mass transfer of hydrogen with the metal. These liquid salt particles nix with the metal and gather H_2.

    - Chlorine destroys the oxide film formed in the gas bubble due to oxygen contamination invariably found with commercial inert gases.[5]

    Establishing the exact mechanism would be difficult, however, the fact that chlorine seems to be more effective than fluorine in aiding hydro-

gen removal indicates that the formation of liquid salts plays a role in the process.

- Alkali Removal

In principle, both chlorine and fluorine should be equally effective for alkali removal while purging molten aluminum. The thermodynamic equilibrium between alkalis dissolved in molten aluminum and these two halogens are shown in Figures 3 and 4 respectively.[1]
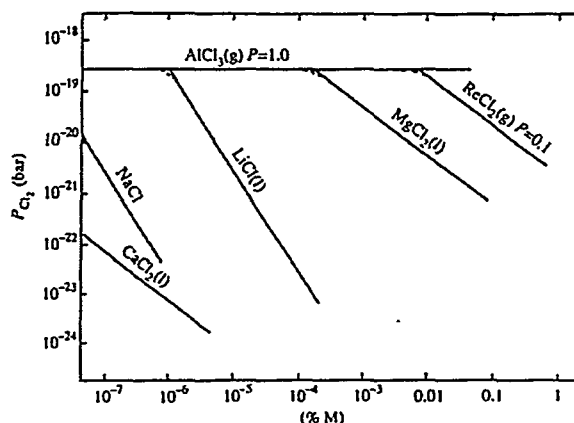
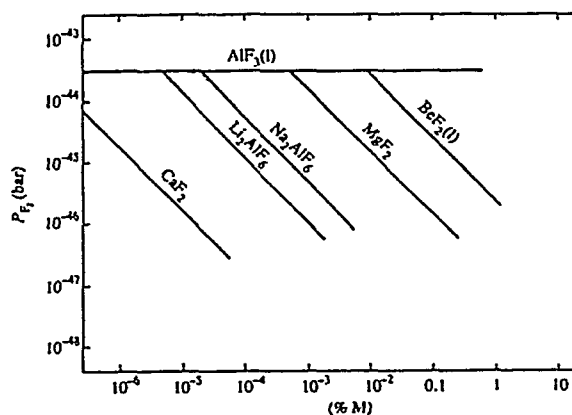Figure 3: Calculated equilibria for ternary Al-M-Cl systems at 1000 K.[1]

Figure 4: Calculated equilibria for ternary Al-M-F systems at 1000 K.[1]

However, practical experience, as shown in detail by Waite and Bernard,[5] indicates that chlorine is more effective. The removal of Ca from molten aluminum by purging in the furnace with either chlorine or sulfur hexafluoride is shown in Figure 5.[5] Calcium removal rate with in-line system using a rotary degasser is shown in Figure 6.[5] Sulfur hexafluoride is much less efficient while furnace fluxing, the difference decreases when using a rotary degasser.
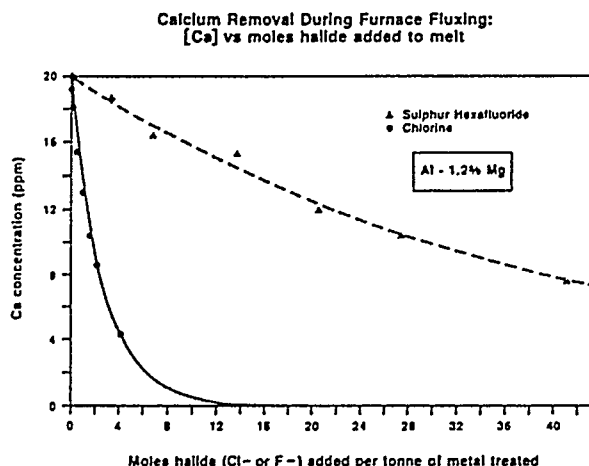
Once again, the higher effectiveness of chlorine is probably related to the presence of liquid $MgCl_2$ salt particles. Waite and Bernard suggested the use of Cl_2-SF_6 mixtures, and tested the ability of these mixtures to remove alkalis. The Cl_2-SF_6 mixtures have efficiency comparable to pure chlorine,[5] as shown in Figure 7.

Figure 5: Calcium concentration during furnace fluxing as a function of the quantity of halogen injected per ton of metal.[5]
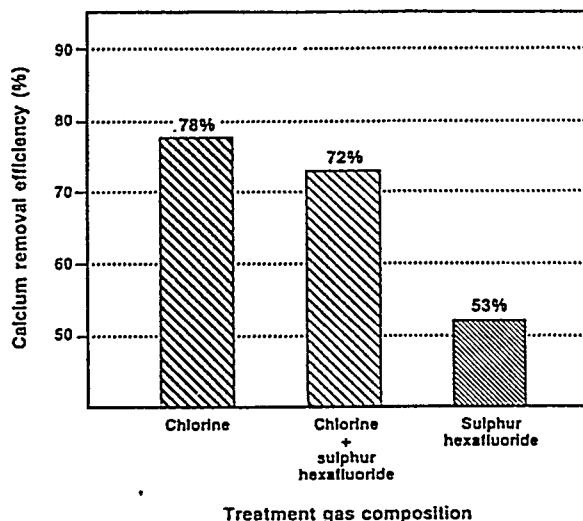
Figure 7: Typical in-line calcium removal efficiencies for different gas mixtures.[5]

- **Inclusion Removal**

The role of reactive gases on inclusion removal during purging of aluminum was discussed previously by several authors. Martins et.al.[7] summarized some practical observations and proposed a mechanism for the contribution of reactive gases to this process.

- Some practical observations have shown that Ar produced a drier dross and cleaner metal than N2.

- The presence of reactive gases generated a drier dross and cleaner metal.

These authors proposed a mechanism where aluminum nitride is formed whenever aluminum is oxidized in air or nitrogen is used for purging. AIN is wetted by molten aluminum, which leads to a wet dross.
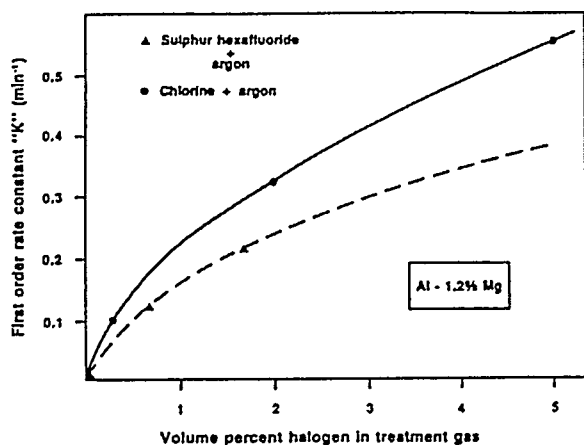
Figure 6: Variation of first order calcium removal rate constant with halogen concentration on the purging gas for rotary degassing.[5]

Other authors[3,5] studied quantitatively the role of reactive gas on inclusion removal. The following observations summarizes their findings.

- Chlorine is the most effective reactive gas.

- Sulfur Hexafluoride is less effective than chlorine.

- Cl_2-SF_6 is as efficient as pure chlorine.

These findings are well illustrated in Figure 8, from the work of Waite and Bernard.[5] Once again, the formation of liquid salt particles seems to play a major role in the removal process.
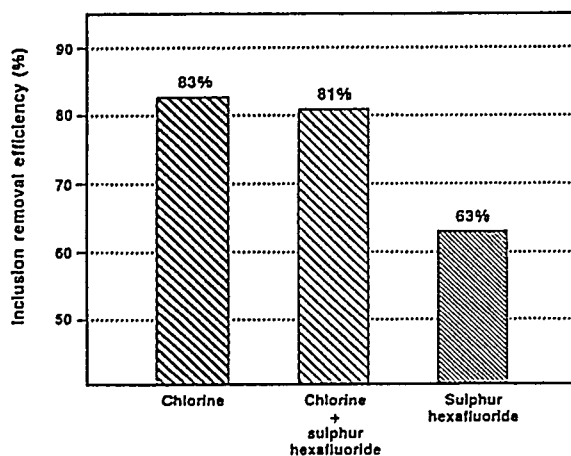
Figure 8: Typical in-line inclusion removal efficiencies for different gas mixtures.[5]

• Formation of Liquid Salts

Several authors have reported the presence of molten salts while purging molten aluminum with chlorine. The beneficial effects of these liquid salt particles on the removal of hydrogen, alkali and inclusions was extensively discussed in the previous sections. However, these liquid salt particles have some deleterious effects which have to be dealt with.

- Lower filtration efficiency. Liquid salts can lower significantly the filtration efficiency of inclusions in molten aluminum. This was well documented by Eady et.al. [6]

- Generate a crusty layer. A thick crusty oxide-molten salt layer is formed in the trough after in-line degasser when molten salts are present.[8] This leads to higher melt losses and eventually pieces of the crusty layer may release and reach the final product.

- Generate oxide patches. Black oxide patches are formed on the surface of sheet ingots, which leads to additional scarfing before rolling.[5]

Obviously having the liquid salt particles on an in-line degasser is beneficial to the purging processes. However, methods to eliminate these particles after the degasser are also essential.

- Carefully control amount of chlorine used on degasser. Operation of the degasser with 0.5% chlorine on the first stage and no chlorine on the second stage can produce salt-free metal. However, this method is not very robust, any turbulence or minor deviation from the prescribed operating practice can lead to salt releases from the degasser.

- Filter liquid salts out. This method was proposed by Gesing et al.[9], However the high cost associated with this practice ($5.00/ton. Al) has made its application impractical so far.

- Use Cl_2-SF_6 mixtures. This method was presented as a solution by two authors.[5,8] The authors believe that the mechanism is that MgF_2 formed when sulfur hexafluoride is used added to chlorine, attaches itself to the liquid salt and transform it into a solid-like agglomerate.

Summary and Conclusions

The role of reactive gases on purging molten aluminum was discussed. Chlorine, fluorine or both are used to aid hydrogen, alkali and inclusion removal.

Chlorine is more effective than fluorine, this fact has been explained as resulting from the formation of liquid $MgCl_2$ salt particles when chlorine is present. The molten salt greatly aid removal of hydrogen, alkalis and inclusions.

However, these liquid salt particles may cause loss of filtration efficiency, formation of a crusty layer on top of liquid metal and generate oxide patches on the surface of cast ingots. Elimination of liquid salt particles downstream of the purging process is required. Liquid salts can be eliminated by limiting the amount of chlorine used, filtering liquid salts or using Cl_2-SF_6 mixtures, as a small addition of SF_6 can remove the liquid salt particles.

Careful control of chlorine addition is practiced by several cast shops, others use Cl_2-SF_6 mixtures, no commercial application of liquid salt filtration has been reported thus far.

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